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A COMPARISON OF MATHEMATICAL MODELS FOR THE PREDICTION OF LNG DENSITIES

Robert D. McCarty

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Prepared for:
American Gas Association, Inc.
1515 Wilson Boulevard
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A COMPARISON OF MATHEMATICAL MODELS FOR THE PREDICTION OF LNG DENSITIES*

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Four mathematical models of the equation of state for LNG like mixtures are compared. Each model has been optimized to the same experimental data set. The experimental data consist of over 175 new PVTx data points taken in this laboratory. The objective of the study was to obtain a mathematical model which would predict LNG densities to within 0.1% of the true value. The extent to which the objective has been achieved is not clear at this time. Additional experimental data are needed to resolve some discrepancies between the present data and all models investigated to date. Computer program listings for all four models are presented.

Key words: Computer program; density; equation of state; LNG; mixtures; PVTx.

1. Introduction

The purpose of this study was to optimize and compare several different mathematical models using the experimentally determined PVTx density data of Haynes, et al. (1976), Haynes and Hiza (1976), Hiza, et al. (1976) and Hiza (1976). These data are for the liquid phase of methane, ethane, propane, normal butane, isobutane and nitrogen and various mixtures thereof. The temperature range of the correlations was limited (95-150 K) and the pressures to those of saturation, the range of which was about 0 to 20 atmospheres. The goals of the study were to produce one or more computer models which would predict a density of LNG (liquefied natural gas) to within 0.1% of the true value, when the temperature, pressure and composition of the LNG are specified. The goal of predicting LNG densities with an accuracy of 0.1% has most probably been achieved. The data from the above references include nine multicomponent (three or more components) mixtures in addition

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to the binary mixture data in Appendix A. One of the methods (the extended corresponding states) predicts all of the densities to within the 0.1% objective except in the case of the methane-normal butane data on page 18 and one point of the propane-nitrogen data on page 22. Haynes, et al. (1976) estimate the uncertainty of these data to be greater than that of the other binary data. A comparison with an independent set of mixture data (68 data points) for mixtures of the same components due to Rodosevich (1973) resulted in no deviations between experimental and predicted (using extended corresponding states) densities greater than 0.1% (see Appendix A). The Rodosevich data include binary mixtures data for the methane-normal butane system.

The choice of models to use in this study was a difficult one, because there are many possible models and methods to chose from. Since no mathematical model is suitable for every need and needs vary greatly from application to application, an effort was made to choose the models to be tested in such a way as to provide useful information to as diversified an audience as possible and still achieve the stated objective of the study. In an effort to achieve these ends, the choice of models was made on the basis of the following criteria: popularity, degree of complexity, type of approach and likelihood of success, with of course the likelihood of success being the most important factor of consideration.

The models and/or methods which are considered here are: the extended corresponding states method (Leach, 1967 and Rowlinson and Watson, 1969); a hard sphere model by Rodosevich and Miller (1975); a cell model proposed by Echert, et al. (1967) as modified by Albright (1973); and a graphical method by Klosek and McKinley (1968). All of the optimization and testing was performed in the Cryogenics Division of NBS at Boulder, Colorado except in the case of the cell model which was done by M. A. Albright at Phillips Petroleum in Bartlesville, Oklahoma. The details of the optimization of the cell model will be published by Albright (1976) elsewhere.

A general discussion of the performance of each model is given in the following sections. A separate section is devoted to each model considered. The appendicies give comparisons of calculated and experimental densities for all the models as well as listings of the computer programs for each model.

2. Extended Corresponding States Method

This method was selected because it seemed to offer an excellent possibility for achieving the objective of predicting the densities of LNG to within 0.1% of the true value.

The extended corresponding states method is labeled as a method rather than a model because it differs from the customary meaning of model in that it is not an equation of state but rather a transformation function which maps the equation of state of a fluid into the equation of state of another. The thermodynamic equations for the extended corresponding states method are developed in a paper by Rowlinson and Watson (1969) and only a very brief description will be given here. Leach (1967) developed transformation functions for hydrocarbons which are called shape factor functions. Mollerup (1976) and Mollerup and Rowlinson (1974) combined the earlier work with the equation of state for methane by Goodwin (1974) to produce a computer program to calculate the density of LNG mixtures. This method for calculating the densities of LNG was estimated by Mollerup (1975) to be accurate to 0.1%; however, a copy of the computer program obtained from Mollerup produced densities for LNG-like mixtures which are as much as 3% different from those measured in this laboratory. Figure 1 shows the deviations between the densities from the computer program of Mollerup and the PVTx measurements mentioned earlier. The open circles represent deviations using the Mollerup (1976) computer program and the solid circles show deviations for the same data points using the computer program given in Appendix B, i.e., the same program after optimization to the new data.

The computer program in Appendix B for the calculation of LNG densities based on the extended corresponding states method is an extensive revision of the Mollerup program.

The extended corresponding states method is defined by the following equations:

$$Z_i[P,T] = Z_o[P\, h_{ii,o}/f_{ii,o},\ T/f_{ii,o}] \qquad (1)$$

$$G_i[P,T] = f_{ii,o}\, G_o[P\, h_{ii,o}/f_{ii,o},\ T/f_{ii,o}] - RT\, \ell n(h_{ii,o}) \qquad (2)$$

where Z is the compressibility factor, G is the Gibbs free energy, P is pressure and T is temperature. The subscript o denotes the reference fluid and the subscript i denotes the fluid for which properties are to be obtained via the equation of state for the reference fluid and the transformation functions $f_{ii,o}$ and $h_{ii,o}$. The double subscript ii is introduced now to allow extension of the method to mixtures. The two defining equations (1) and (2) are necessary since there are two transformation functions. In this case the equation of state for methane by McCarty (1974) was chosen for the reference fluid. During the course of the study it was necessary to modify the equation of state by McCarty (1974). The equation of state was modified to give a realistic vapor liquid phase boundary down to a temperature of 43 K. This modification was necessary to accommodate the very low reduced temperatures of the heavier hydrocarbons and was accomplished without changing the performance of the equation of state above the triple point of methane. The equation of state is given in Appendix B.

The $f_{ii,o}$ and $h_{ii,o}$ are defined as

$$f_{ii,o} = (T^c_{ii}/T^c_o)\ \theta_{ii,o}\ (T_r,V_r) \tag{3}$$

and

$$h_{ii,o} = (V^c_{ii,o}/V^c_o)\ \phi_{ii,o}\ (T_r,V_r) \tag{4}$$

where

$$\theta_{ii,o} = 1 + (w_i - w_o)[a_1 - a_2 \ln T_{r_i} + (a_3 - a_4/T_{r_i})(V_{r_i} - a_5)] \tag{5}$$

and

$$\phi_{ii,o} = \frac{Z^c_o}{Z^c_i}\ 1 + (w_i - w_o)[b_1(V_{r_i} - b_2) - b_3(V_{r_i} - b_4) \ln T_{r_i}] \tag{6}$$

The V_{r_i} and T_{r_i} are reduced temperature and volume, (i.e., $T_{r_i} = T/T^c_{ii}$ and $V_{r_i} = V/V^c_{ii}$) and w_i is a fluid dependent parameter estimated using experimental data. The a_j's and b_j's are fluid independent parameters, estimated with experimental data and the Z^c_o/Z^c_i is the ratio of the compressibility factors at the critical point. The parameters a_j, b_j, w_i and Z_{ii} are given in Appendix A. All of these parameters were estimated using the experimental PVT data set from this laboratory and least squares estimation techniques.

The extension of the above to mixtures is now accomplished by the following application of the following combining rules

$$h_{x,o} = \sum_i \sum_j x_i x_j\ h_{ij,o} \tag{7}$$

$$f_{x,o}\ h_{x,o} = \sum_i \sum_j x_i x_j\ f_{ij,o}\ h_{ij,o} \tag{8}$$

$$f_{ij,o} = \xi_{ij}\ (f_{ii,o}\ f_{jj,o})^{1/2} \tag{9}$$

$$h_{ij,o} = \eta_{ij}\ (\tfrac{1}{2} h^{1/3}_{ii,o} + \tfrac{1}{2} h^{1/3}_{jj,o})^3 \tag{10}$$

The ξ_{ij} and the η_{ij} are binary interaction parameters determined by least squares from the PVTx data for binary mixtures. These parameters are given in Appendix A.

This method works quite well as may be seen in the comparisons in Appendix A. It has indeed reproduced all of the present experimental data

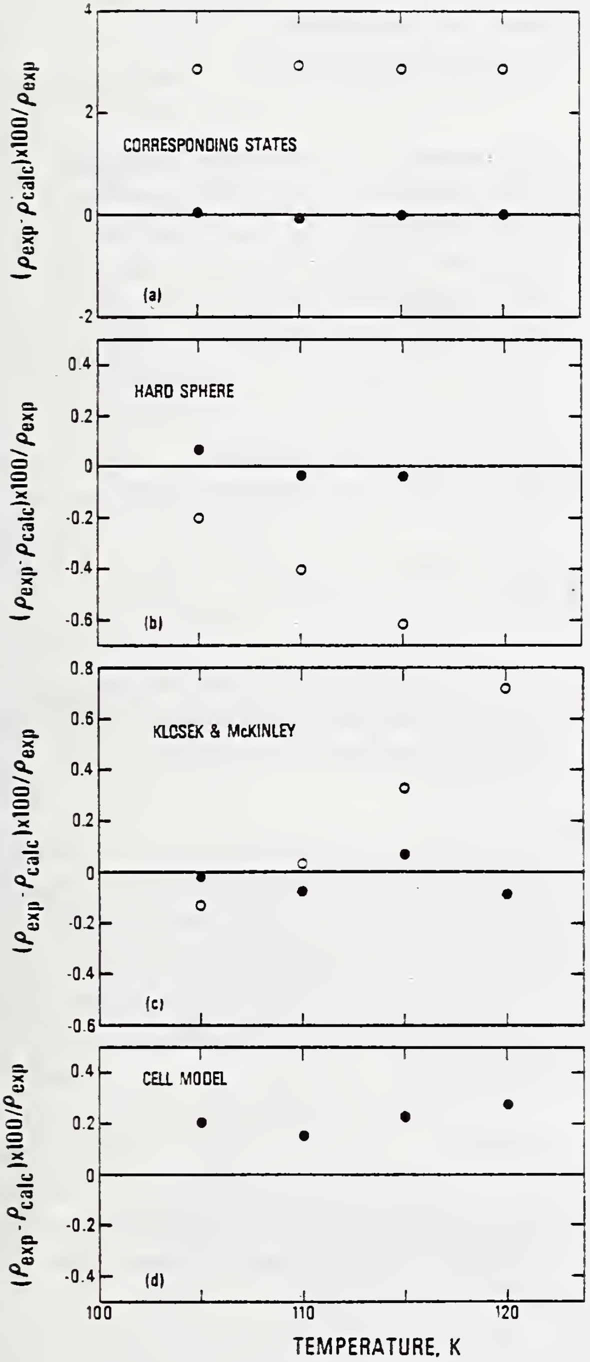

Figure 1. Deviations in density between data from Hiza (1976) and the indicated model. Open circles are for the model before the present work and the closed circles are for the same models after the present work. The composition of the mixture is 0.806 CH_4 + 0.047 C_2H_6 + 0.048 C_3H_8 + 0.050 nC_4H_{10} + 0.049 N_2.

set to within ± 0.1% except for some of the systems containing butane which are strongly suspected to be in error. Since only binary systems data were used as input to the method, the calculated densities for multicomponent data are, in a sense, predictions on the part of the method.

Figure 1 gives a comparison of the extended corresponding states method before and after modification.

Unfortunately the method has some deficiencies. The method is complex and is not easy to use even with the aid of a computer. Figure 1 shows that it does not perform well when insufficient experimental data are available as input since all of the other models tested show deviations which are much less than those in figure 1 when tested before optimization, i.e., as they were taken from the literature. On the advantages side of the comparison, this method has the most versatility, it handles nitrogen as a component in any concentration, it has the widest PVTx range of any of the methods, and it is probably the most accurate for the calculation of densities. It can also be used to calculate other thermodynamic properties including phase equilibria.

A comparison between the data of Rodosevich and predictions by the extended corresponding states method resulted in no deviations greater than 0.1%. These comparisons were made before any of the Rodosevich data were used as input to the optimization process. The CH_4-nC_4H_{10} and the CH_4-iC_4H_{10} data of Rodosevich were used in the final optimization of the corresponding states model. A complete tabulation of deviations between the various models and the Rodosevich data is given in Appendix A.

3. A Hard Sphere Method

This method was selected for consideration since it currently enjoys wide popularity. The model of Rodosevich and Miller (1975) is one of many modifications of the Longuet-Higgins and Widom (1964) model, and was chosen to be included in this study as a representative example of the application of the hard sphere equation of state concept to the correlation of PVTx data. The equation of state by Rodosevich and Miller (1975) is

$$\frac{PV}{RT} = c\,\frac{1 + y + y^2}{(1 - y)^3} - \frac{a}{RTV} \qquad (11)$$

where the $y = b/4V$ and a, b, and c are adjustable parameters, the PVT and R have the usual meaning. The equation is applied to mixtures by assuming the one-fluid theory and applying the following combining rules.

$$a_m = \sum_i \sum_j a_{ij}\, x_i x_j \qquad (12)$$

$$b_m = \sum_i \sum_j b_{ij} x_i x_j \tag{13}$$

$$c_m = \sum_i \sum_j c_{ij} x_i x_j \tag{14}$$

The mixing rules are:

$$b_{ij} = \left[\frac{b_{ii}^{1/3} + b_{jj}^{1/3}}{2} (1 - j_{ij})\right]^3 \tag{15}$$

$$a_{ij} = a_{ii}a_{jj}{}^{1/2} \left[\frac{b_{ij}^2}{b_{ii}b_{jj}}\right]^{1/2} (1 - k_{ij}) \tag{16}$$

$$c_{ij} = \frac{c_{ii} + c_{jj}}{2} \tag{17}$$

The parameters j_{ij} and k_{ij} are in this case the binary interaction parameters. The a's, b's, c's, j_{ij}'s and k_{ij}'s are given in Appendix B. The excess volume is now calculated using the equation of state and

$$V_E = \hat{V}_m - \Sigma \hat{V}_i X_i \tag{18}$$

where $\hat{V}_m$ and the $\hat{V}_i$ are calculated via the equations 11 through 17 and then

$$V_m = \Sigma V_i X_i + V_E \tag{19}$$

where the V_E is from equation (18) and the V_i are from experimental data. The V_i in this case were calculated from the equations for the liquid density of the pure fluids given in Appendix C.

The above equations are those of Rodosevich and Miller (1975) and only the j_{ij}'s and k_{ij}'s have been revised on the basis of the present new data set, and only binary systems data were used to estimate via least squares the j_{ij}'s and k_{ij}'s. An attempt to optimize the a, b and c parameters for each pure fluid was made using the new pure fluid data; however the results were disappointing. No appreciable improvement in the prediction of mixture densities was achieved. The results did indicate, however, that any substantial improvement over the a, b and c values given by Rodosevich and Miller (1975) will require some sort of temperature dependence for those parameters.

Figure 1 gives deviations between calculated and experimental densities for the same mixtures but with different parameters for the model as the means of calculating the densities. The open circles show deviations between calculated and experimental densities before the model was optimized using the present data set. The closed circles represent the deviations for the same data points after optimization. Only binary system data were used in the optimization process. A table of deviations between experimental densities and those calculated via the hard sphere model is given in Appendix A.

The hard sphere model as applied here has some disadvantages when applied to the present problem. The most serious disadvantage is that it is an excess properties method, and therefore when temperatures of the mixture approach the critical temperature of one of the component fluids the method fails. Since the critical temperature of N_2 is about 126 K, calculations for mixtures containing N_2 are limited to temperatures below about 120 K, however at temperatures where the critical temperature of a component does not present a problem, the method works very well. The model is neither the most accurate nor the simplest model investigated, but based on the experience of this study, it is probably the most reliable to extrapolate.

4. A Revised Klosek and McKinley Method

This method (Klosek and McKinley, 1968) is included in the study because it is currently very popular and it seemed at the outset to perform about as well as any of the others chosen. In addition it is one of the easiest methods to apply.

This method is a totally empirical recipe for calculating the density of a LNG-like mixture given the temperature and composition. Pressure is not taken into account. However, this does not seem to be a serious omission. The procedure proposed by Klosek and McKinley (1968) is as follows:

$$V_{mix} = \Sigma X_i V_i - k X_{CH_4} \qquad (20)$$

where V_{mix} is the volume of the mixture, X_i and V_i are the mole fraction and volume of the ith component, X_{CH_4} is the mole fraction of methane and k is a correction factor obtained from a table or graph. The V_i and k are obviously temperature dependent and in addition k is dependent upon the molecular weight of the mixture.

Using the present data set k was calculated for all of the experimental data points where methane was present in the mixture and excluding all data points where N_2 was present in greater than 5% concentration. Figure 2 shows a typical isotherm for k. All of the isotherms available show similar behavior, i.e., all of the k's for mixtures containing nitrogen (of about 5%) fall on one line and all of those for mixtures without nitrogen fall on another. Since all of the mixtures with nitrogen have about the same amount of nitrogen present (about 4.5%), the method was modified by adding a term

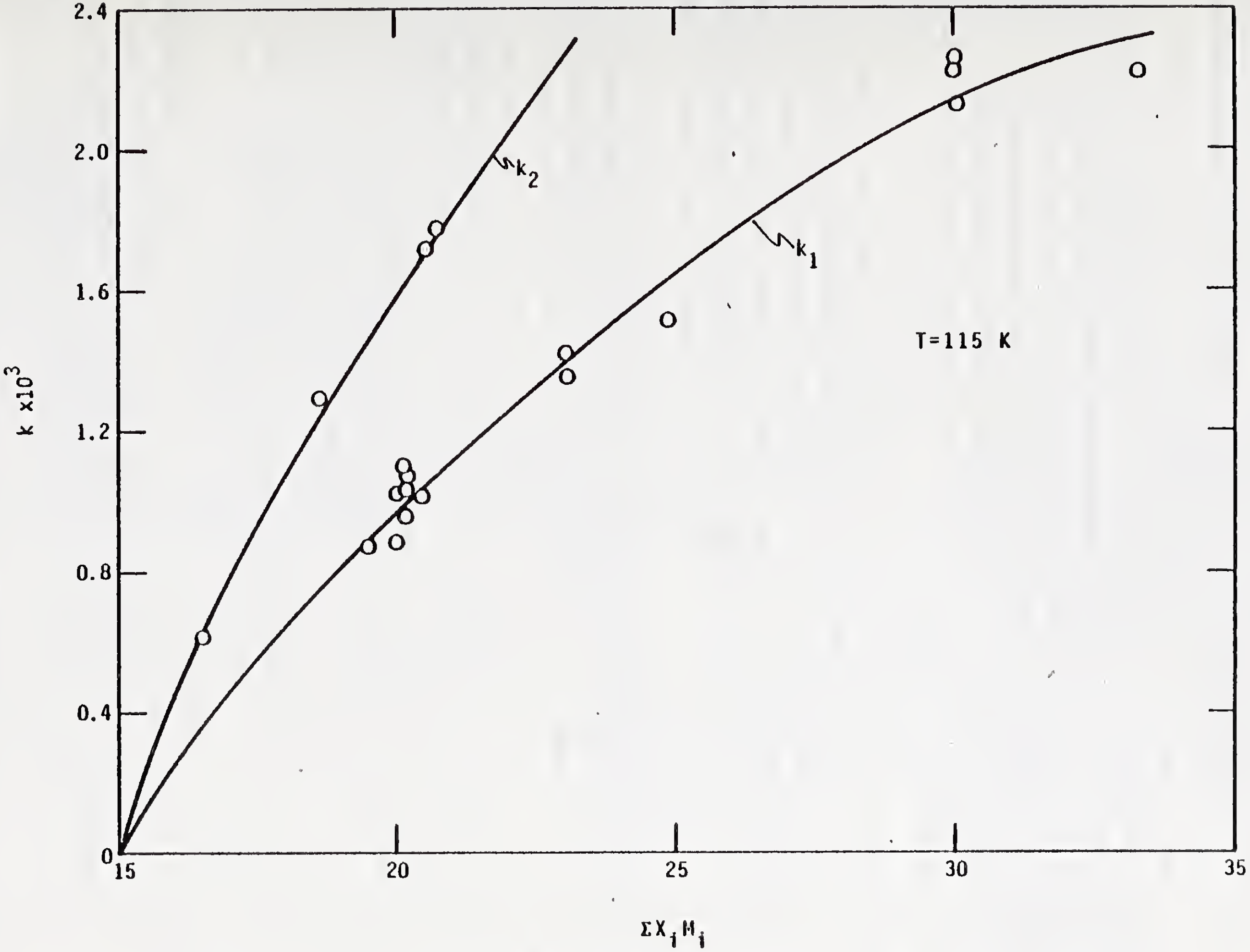

Figure 2. A plot of the correction factors (k_1 and k_2) for the 115 Kelvin Isotherm.

to take into account the nitrogen when it is present. The equation becomes

$$V_{mix} = \Sigma X_i V_i - [k_1 + (k_2 - k_1) X_{N_2}/.0425] X_{CH_4} \qquad (21)$$

where everything is the same as in equation (20) except the k_1 is read from one curve and k_2 is read from the other. Appendix D gives tables of values for the V_i, k_1 and k_2 which are spaced such that linear interpolation is adequate in both variables (i.e., temperature or molecular weight). Using the experimental data it was possible to calculate k directly for the 105, 110, 115, 120 and 125 kelvin isotherms only. A comparison of the linear extrapolation of k to both lower and higher temperatures indicated the extrapolation to be unsatisfactory. Consequently values of k for the 90, 95, 100, 130, and 135 K isotherms were calculated using the extended corresponding states model in section 2.

In the process of calculating k for these additional isotherms it was discovered that for mixtures containing only methane-ethane and propane a table of k's could be constructed to give values for density almost identical to those of the corresponding states model in section 2, but when either butane or nitrogen were added k became composition dependent. Consequently, it was decided to construct the k_1 and k_2 tables in Appendix C such that they would give results similar to the corresponding states method for methane-ethane and propane mixtures and give the best results for mixtures containing the butanes where the concentrations of the butanes were 5% or less (total) and where the concentration of nitrogen is also less than 5%. The computer comparison of the two models also revealed the following limitation. For the model to predict LNG densities to an accuracy of 0.15% or better, the mixture must contain 80% or more methane and less than 5% butane and nitrogen.

Figure 1 allows a common basis of comparison with the methods given in the other sections. The open circles represent the deviations before optimization and the solid circles show deviations after optimization. The optimization for this model was accomplished with multicomponent data as well as binary mixture data. An extensive tabulation of deviations between calculated and experimental densities is given in Appendix A.

For the purpose of calculating the density of LNG like mixtures, the revised Klosek and McKinley method presented here has one very real advantage over all the others, and that is, it is simple. It is quite easy for almost anyone to use the tables in Appendix C to arrive at an LNG density using only pencil and paper. This is not true of any of the other methods. The value of density arrived at in this manner will be within about 0.15% of the true value in the worst case, and if the composition of the LNG has little or no butane or nitrogen in it, the density will be much better, on the order of

0.1% of the true value. There are, however, some disadvantages. It does not handle nitrogen or butane as a component as well as some of the other methods and if over 5% of either nitrogen or butane is present, it departs rapidly from measured values. It is not as accurate as the extended corresponding states method and it does not extrapolate well.

5. The Cell Model

The cell model considered here was originally proposed by Renon, et al. (1967). In a paper by the same three authors which appeared simultaneously (Eckert, et al., 1967), the cell model was applied to mixtures via Scott's (Scott, 1956) two-fluid theory and a three parameter corresponding states theory. Albright (1973) further modified the method by modifying the mixing rules on the basis of a proposal by Yuan (1971) and by inserting a pressure dependence based on the experimental liquid ethane data by Pope (1971).

As mentioned in the introduction, the optimization of this method was carried out by M. Albright (1976) at Phillips Petroleum Company in Bartlesville, Oklahoma and the details of this work will be published elsewhere. A listing of the optimized computer program together with a comparison with the experimental data are given in Appendices E and A respectively.

Figure 1 shows deviations between densities calculated using the cell model and experimental densities. The experimental densities are those used in the comparisons in the previous sections.

6. Conclusions

As stated earlier the objective of this study was to produce one or more mathematical models which will predict the density of LNG to within 0.1% of the true value. This objective has most probably been achieved as is demonstrated by the ability of the models to predict the experimental PVTx data for LNG-like mixtures to within 0.1%; however all of the four models have been fit to the data of Haynes, et al. (1976) who report that their data may have as much as 0.05% systematic error. Therefore, it is estimated that the densities of LNG-like mixtures as calculated from any one of the four models given here will be within 0.15% of the true density for that mixture.

Each of the models has its particular advantages and disadvantages. The extended corresponding states model has the widest range of pressure, temperature and composition and is probably the most accurate, but it is complex and difficult to use.

The revised Klosek and McKinley method is the easiest to use but it is severely limited in range of composition and temperature (i.e., less than 5% nitrogen or butane).

The hard sphere model works well but is limited to temperatures below 120 K for mixtures containing nitrogen.

The cell model also works well, but does not handle nitrogen at high concentrations (30% or more) as well as the extended corresponding states, and is only slightly less complex.

The last page of Appendix A is a comparison of the performance of various models for actual LNG compositions. The comparison shows that the models perform equally well until the concentration of the butanes exceeds 4%. The largest disagreement between models occurs for the mixture which contains a total of 4.3% of iC_4H_{10} and nC_4H_{10} where the difference between the cell model and the revised Klosek and McKinley method is 0.2%.

All of the other predictions for the other four compositions are within 0.11% of each other, and one of these mixtures includes 2.6% of the butane. It is true that all of these methods were optimized using the same data set, but the methods do differ radically in some cases and one of them (corresponding states) does agree well (0.1%) with the Rodosevich data which represents an independent check. Unfortunately an exhaustive search of the world's literature has not revealed any additional experimental data of compositions which are of interest here and which are of sufficient accuracy and precision to be of use in this correlation, either as input data or as an independent check.

More measurements of LNG like multicomponent mixtures have been scheduled to more precisely determine the concentration limits of nitrogen and butane.

At the request of sponsor, the pentanes (iso and normal) have been added as a possible component in the mixture. These components have been added on the basis of the pure fluid data of Orrit and Olives (1974) only, and no estimate of accuracy of the calculated density for mixtures containing pentane is possible.

7. References

Albright, M. A., Private communication (1976).

Albright, M. A., A Model for the Precise Calculation of Liquefied Natural Gas Densities, NGPA Technical Publication TP-3 (1973).

Eckert, C. A., Renon, H. and Prausnitz, J. M., Molecular Thermodynamics of Simple Liquids, IEC Fund 6, 58 (1967).

Goodwin, R. D., The Thermophysical Properties of Methane, from 90 to 500 K at Pressures up to 700 Bars, Nat. Bur. Stand. (U.S.), Tech. Note 653 (1974).

Haynes, W. M., Hiza, M. J. and Frederick, N. V., A Magnetic Suspension Densimeter for Measurements on Fluids of Cryogenic Interest, Review of Scientific Instruments 47, No. 10, 1237-50 (Oct 1976).

Haynes, W. M. and Hiza, M. J., Measurements of the Orthobaric Liquid Densities of Methane, Ethane, Propane, Isobutane, and Normal Butane, J. Chem. Thermodyn., in press, 1976.

Hiza, M. J., Haynes, W. M. and Parrish, W. R., Orthobaric Liquid Densities and Excess Volumes for Binary Mixtures of Low Molecular Weight Alkanes and Nitrogen Between 105 and 140 K, in preparation, 1976.

Hiza, M. J., Private communication on Orthobaric Liquid Densities of Multicomponent Mixtures, 1976.

Klosek, J. and McKinley, C., Densities of Liquefied Natural Gas and of Low Molecular Weight Hydrocarbons, Proc. First Int. Conf. on LNG, IGT, Chicago (1968).

Leach, J. W., Molecular Structure Correction for Applying the Theory of Corresponding States to Non-Spherical Pure Fluids and Mixtures, Ph.D. Thesis, Rice University (1967).

Longuet-Higgins, H. C. and Widom, B., A Rigid Sphere Model for Melting of Argon, Mol. Phys. 8, 549 (1964).

McCarty, R. D., A Modified Benedict-Webb-Rubin Equation of State for Methane Using Recent Experimental Data, Cryogenics 14, No. 5, 276-80 (May 1974).

Mollerup, J. and Rowlinson, J. S., The Prediction of Densities of Liquefied Natural Gas and of Lower Molecular Weight Hydrocarbons, Chem. Engng. Sci. 29 (1973).

Mollerup, J., Correlated and Predicted Thermodynamic Properties of LNG and Related Mixtures in the Normal and Critical Region, Adv. Cryog. Eng. 20, 172 (1975).

Orrit, J. and Olives, J. F., Density of Liquefied Natural Gas and Its Components. Distributed at the 4th International Conference on Liquefied Natural Gas, Algeria (1974).

Pope, G. A., Calculation of Argon, Methane and Ethane Virial Coefficients at Low Reduced Temperature, Ph.D. Thesis, Rice University (1971).

Renon, H., Eckert, C. A. and Prausnitz, J. M., Molecular Thermodynamics of Simple Liquids, IEC Fund. 6, 52 (1967).

Rodosevich, J. B. and Miller, R. C., Calculation of LNG Excess Volumes by a Modified Hard-Sphere Model, Adv. Cryog. Eng. 19, 339 (1974).

Rodosevich, J. B., Measurements and Prediction of Liquefied Natural Gas Densities, M.Sc. Thesis, Univ. Wyoming (1973).

Rowlinson, J. S. and Watson, I. D., The Prediction of the Thermodynamic Properties of Fluids and Fluid Mixtures - I. The Principle of Corresponding States and its Extensions, Chem. Engng. Sci. 24, 1565 (1969).

Scott, R. L., J. Chem. Phys. 25, 193 (1956).

Yuan, I. C., Correlation and Prediction of Excess Properties for Selected Binaries in the C_6-C_7 Hydrocarbon Boiling Range of Conformal Solution Theory, D. SC. Dissertation, Washington University (1971).

Appendix A. Deviation Tabulations

The deviations tabulated below have been calculated in every case using the following convention:

$$\% \text{ Deviation} = 100\ (D_{exp} - D_{cal})/D_{exp}$$

where D is density in moles/liter, the subscripts exp and cal stand for experimental, and calculated via the model indicated. No entry is given for a particular model when the calculation is not appropriate for that model.

In the case of the corresponding states model there is a deviation tabulated for every data point. For the hard sphere model no deviations are tabulated for the pure fluid data points because the method is an excess volume method and other models were used to calculate the so called ideal volume, i.e., $V_{Ideal} = \Sigma X_i V_i$ (see Appendix B). For the revised Klosek and McKinley method deviations have been tabulated for only those mixture data points which contain methane and have less than 5% nitrogen. This is also an excess volume method and the calculation of the ideal volume is outlined in Appendix C.

Saturated Liquid Ethane
(Molecular Weight 30.07012)

	Experimental			% Deviation		
Pressure atm	Density mol/ℓ	Temperature K	Corresponding States	Hard Sphere	Revised Klosek and McKinley	Cell Model
0.000	21.3408	100.	0.02			-0.07
0.000	21.1585	105.	0.01			-0.03
0.001	20.9746	110.	0.00			-0.00
0.002	20.7927	115.	0.00			0.01
0.004	20.6022	120.	-0.03			0.05
0.007	20.4186	125.	-0.02			0.05
0.013	20.2317	130.	-0.02			0.04
0.023	20.0461	135.	-0.00			0.02
0.038	19.8566	140.	0.00			0.00

Saturated Liquid Propane
(Molecular Weight = 44.09721)

0.000	16.3065	100.075	0.01			-0.07
0.000	16.1872	105.075	-0.01			-0.01
0.000	16.0718	110.075	-0.01			-0.01

Saturated Liquid Propane (Continued)

(Molecular Weight = 44.09721)

	Experimental			% Deviation		
Pressure atm	Density mol/ℓ	Temperature K	Corresponding States	Hard Sphere	Revised Klosek and McKinley	Cell Model
0.000	15.9557	115.075	-0.00			0.03
0.000	15.8411	120.075	0.01			0.03
0.000	15.7250	125.075	0.01			0.04
0.000	15.6085	130.075	0.01			0.03
0.000	15.4910	135.075	-0.00			0.03
0.000	15.3751	140.075	0.00			-0.00

Saturated Liquid Normal Butane

(Molecular Weight = 58.1243)

0.000	12.6517	135.075	-0.03			-0.01
0.000	12.5706	140.075	-0.02			0.01
0.000	12.4920	145.075	0.01			-0.00

Saturated Liquid Isobutane

(Molecular Weight = 58.1243)

0.000	12.7305	115.075	-0.01			-0.01
0.000	12.6489	120.075	-0.00			0.00
0.000	12.5687	125.075	0.02			-0.00
0.000	12.4850	130.075	0.01			0.02
0.000	12.4015	135.075	-0.00			0.02
0.000	12.3215	140.075	0.02			-0.01
0.000	12.2353	145.075	-0.01			0.01

Saturated Liquid Nitrogen

(Molecular Weight = 28.0134)

5.257	25.6624	95.075	0.02			0.05
7.715	24.6207	100.075	-0.02			0.00
10.744	23.4841	105.075	0.01			-0.08
14.544	22.1840	110.075	0.00			0.06
19.222	20.6490	115.075	0.01			1.93
21.927	19.7356	117.575	0.02			5.22
24.898	18.6525	120.075	0.02			8.64

Methane-Ethane Mixtures

Pressure atm	Experimental		% Deviation			
	Density mol/ℓ	Temperature K	Corresponding States	Hard Sphere	Revised Klosek and McKinley	Cell Model
$0.35457\ CH_4 + 0.64543\ C_2H_6$						
0.252	23.1032	105.	-0.07	-0.05		-0.04
0.387	22.8777	110.	-0.05	-0.04		-0.05
0.572	22.6478	115.	-0.03	-0.02		-0.05
0.815	22.4035	120.	-0.07	-0.06		-0.11
1.131	22.1872	125.	0.03	0.04		-0.02
1.53	21.9441	130.	0.02	0.03		-0.03
$0.49325\ CH_4 + 0.50675\ C_2H_6$						
0.321	23.9619	105.	0.07	0.07		0.10
0.496	23.6937	110.	0.03	0.03		0.03
0.739	23.4328	115.	0.03	0.01		0.01
1.06	23.1559	120.	-0.03	-0.02		-0.06
1.49	22.8933	125.	-0.00	0.00		-0.04
2.02	22.6290	130.	0.03	0.04		-0.01
2.69	22.3581	135.	0.05	0.06		0.02
3.51	22.0765	140.	0.04	0.05		0.03
$0.68006\ CH_4 + 0.31994\ C_2H_6$						
0.411	25.1027	105.	0.07	0.05	0.09	0.08
0.637	24.7802	110.	0.01	-0.01	0.04	0.00
0.950	24.4612	115.	-0.03	-0.04	0.00	-0.04
1.36	24.1402	120.	-0.05	-0.06	-0.02	-0.06
1.90	23.8212	125.	-0.05	-0.05	-0.01	-0.05
2.59	23.5007	130.	-0.02	-0.01	0.02	-0.00
Methane Propane Mixtures						
$0.29538\ CH_4 + 0.70462\ C_3H_8$						
0.267	18.5132	105.	-0.12	-0.08		-0.08
0.404	18.3624	110.	-0.12	-0.09		-0.12

$0.49637\ CH_4 + 0.50363\ C_3H_8$

	Experimental			% Deviation		
Pressure atm	Density mol/ℓ	Temperature K	Corresponding States	Hard Sphere	Revised Klosek and McKinley	Cell Model
0.379	20.4909	105.	-0.03	0.01		0.02
0.584	20.3046	110.	-0.03	0.01		-0.01
0.863	20.1180	115.	-0.02	0.01		-0.03
1.23	19.9311	120.	0.00	0.01		-0.04
1.700	19.7471	125.	0.04	0.03		-0.02
2.29	19.5546	130.	0.05	0.01		-0.03

$0.74920\ CH_4 + 0.25080\ C_3H_8$

0.472	23.4768	105.	-0.02	0.02	-0.11	0.02
0.728	23.2064	110.	-0.03	0.00	-0.13	-0.02
1.085	22.9364	115.	-0.02	-0.00	-0.13	-0.03
1.561	22.6665	120.	0.01	0.01	-0.12	-0.01
2.187	22.3818	125.	-0.01	-0.04	-0.16	-0.03
2.989	22.1019	130.	0.01	-0.05	-0.14	-0.01

$0.85796\ CH_4 + 0.14204\ C_3H_8$

0.510	24.9622	105.	0.07	0.10	-0.02	0.09
0.791	24.6331	110.	0.06	0.08	-0.03	0.07
1.183	24.2941	115.	0.03	0.04	-0.08	0.03
1.70	23.9491	120.	-0.00	-0.00	- .11	0.01
2.383	23.5941	125.	-0.05	-0.06	-0.19	-0.02
3.257	23.2461	130.	-0.04	-0.06	-0.19	0.01

Methane Normal Butane Mixtures

$0.91674\ CH_4 + 0.08326\ nC_4H_{10}$

.514	25.1536	105.	0.23	0.25	0.16	0.30
.799	24.7960	110.	0.15	0.16	0.09	0.16
1.200	24.4512	115.	0.15	0.14	0.08	0.10
1.730	24.0910	120.	0.11	0.08	0.04	0.00
2.440	23.7370	125.	0.12	0.08	0.05	-0.03
3.330	23.3789	130.	0.15	0.08	0.06	-0.04
4.450	23.0110	135.	0.17	0.08	0.09	-0.04
5.810	22.6391	140.	0.21	0.10	0.21	-0.02

	Experimental			% Deviation		
Pressure atm	Density mol/ℓ	Temperature K	Corresponding States	Hard Sphere	Revised Klosek and McKinley	Cell Model
$0.58828\ CH_4 + 0.41172\ nC_4H_{10}$						
1.615	18.6495	120.	0.00	0.00		0.09
2.251	18.4772	125.	-0.02	- .02		-0.05
2.251	18.4853	125.	0.03	0.03		-0.01
3.141	18.3058	130.	-0.03	-0.07		-0.19
Methane Isobutane Mixtures						
$0.48687\ CH_4 + 0.51313\ iC_4H_{10}$						
0.621	17.3575	110.	0.02	0.07		-0.02
0.926	17.2076	115.	-0.01	-0.00		-0.05
1.343	17.0639	120.	-0.01	-0.03		-0.03
1.828	16.9156	125.	-0.03	0.10		-0.03
Methane-Nitrogen Mixtures						
$0.95248\ CH_4 + 0.04752\ N_2$						
1.36	26.8476	105.	-0.03	-0.05	-0.06	-0.05
1.96	26.4052	110.	0.04	0.00	0.04	0.00
2.600	25.9374	115.	0.05	0.01	-0.07	0.02
3.45	25.4522	120.	0.06	failed	-0.02	0.03
4.54	24.9496	125.	0.07	failed	0.03	0.04
5.75	24.4210	130.	0.04	-5.69	0.02	0.03
7.20	23.8600	135.	-0.03	-4.00	0.01	-0.01
9.08	23.2809	140.	-0.07	-2.69		-0.02
$0.69651\ CH_4 + 0.30349\ N_2$						
3.40	26.8735	100.	-0.00	0.06		0.09
4.600	26.3393	105.	0.04	0.02		0.07
6.100	25.7686	110.	-0.00	-0.05		-0.02
7.91	25.1790	115.	-0.03	0.13		-0.08
9.980	24.5737	120.	-0.04	1.88		-0.07
$0.50758\ CH_4 + 0.49242\ N_2$						
3.260	27.0801	95.	0.04	0.08		0.13
4.59	26.4588	100.	0.02	-0.05		0.04
6.29	25.8106	105.	-0.02	-0.18		-0.06
8.33	25.1387	110.	-0.05	- .21		-0.10

$0.50758\ CH_4 + 0.49242\ N_2$ (continued)

	Experimental			% Deviation		
Pressure atm	Density mol/ℓ	Temperature K	Corresponding States	Hard Sphere	Revised Klosek and McKinley	Cell Model
10.83	24.4431	115.	-0.03	.24		-0.05
13.800	23.7096	120.	-0.03	3.37		0.07
17.08	22.9315	125.	-0.01	failed		0.25
20.820	22.1005	130.	0.08	-2.29		0.05

Ethane-Propane Mixtures

$0.67287\ C_2H_6 + 0.32713\ C_3H_8$

Pressure atm	Density mol/ℓ	Temperature K	Corresponding States	Hard Sphere	Revised Klosek and McKinley	Cell Model
0.000	18.619	125.	0.00	0.02		-0.02
0.000	18.4646	130.	0.01	0.02		-0.00
0.000	18.3059	135.	0.00	0.01		0.00
0.000	18.1509	140.	0.02	0.01		0.05

$0.50105\ C_2H_6 + 0.49895\ C_3H_8$

Pressure atm	Density mol/ℓ	Temperature K	Corresponding States	Hard Sphere	Revised Klosek and McKinley	Cell Model
0.000	18.3618	105.	0.02	0.02		0.04
0.000	18.2169	110.	0.00	0.01		0.00
0.000	18.0726	115.	-0.01	-0.00		-0.02
0.000	17.9282	120.	-0.01	-0.01		-0.04
0.000	17.7880	125.	0.00	0.00		-0.03
0.000	17.6412	130.	-0.02	-0.02		-0.04
0.000	17.4988	135.	-0.01	-0.01		-0.01
0.000	17.3526	140.	-0.01	-0.03		0.00

Ethane Normal Butane Mixtures

$0.65343\ C_2H_6 + 0.34657\ nC_4H_{10}$

Pressure atm	Density mol/ℓ	Temperature K	Corresponding States	Hard Sphere	Revised Klosek and McKinley	Cell Model
0.000	17.2184	115.	0.00	-0.00		0.00
0.000	17.0824	120.	-0.01	-0.02		-0.03

$0.67117\ C_2H_6 + 0.32883\ nC_4H_{10}$

Pressure atm	Density mol/ℓ	Temperature K	Corresponding States	Hard Sphere	Revised Klosek and McKinley	Cell Model
0.000	17.5047	110.	0.00	-0.00		0.01
0.000	17.3706	115.	0.00	0.01		-0.00
0.000	17.1031	125.	0.01	0.02		-0.01
0.000	16.9626	130.	-0.02	-0.01		-0.04
0.000	16.8285	135.	-0.01	-0.00		-0.01
0.000	16.6947	140.	0.01	0.00		0.03

Ethane Isobutane Mixtures

	Experimental			% Deviation		
Pressure atm	Density mol/ℓ	Temperature K	Corresponding States	Hard Sphere	Revised Klosek and McKinley	Cell Model
$0.68939\ C_2H_6 + 0.31061\ iC_4H_{10}$						
0.000	17.3716	115.	-0.00	-0.01		-0.03
0.000	17.2344	120.	-0.02	-0.03		-0.05
$0.72436\ C_2H_6 + 0.27564\ iC_4H_{10}$						
0.000	17.9779	105.	0.00	0.01		0.00
0.000	17.8401	110.	0.01	0.01		-0.01
0.000	17.4235	125.	0.01	0.01		-0.01
0.000	17.2825	130.	0.00	0.00		0.00
Ethane Nitrogen Mixtures						
$0.94067\ C_2H_6 + 0.05933\ N_2$						
3.800	21.4718	105.	-0.03	-0.02		-0.01
4.57	21.2912	110.	0.03	0.03		0.03
5.400	21.0845	115.	-0.04	-0.01		-0.03
6.300	20.8998	120.	0.00	-0.72		0.02
Propane Normal Butane Mixtures						
$0.58692\ C_3H_8 + 0.41308\ nC_4H_{10}$						
0.000	14.6839	110.	0.01	0.02		0.04
0.000	14.1748	135.	-0.03	-0.03		-0.06
0.000	14.0786	140.	0.00	-0.00		-0.02
$0.60650\ C_3H_8 + 0.39350\ nC_4H_{10}$						
0.000	14.1343	140.	-0.00	-0.00		-0.02
0.000	14.0333	145.	-0.00	-0.00		-0.00
0.000	13.9345	150.	0.02	0.02		0.05
$0.60949\ C_3H_8 + 0.39051\ nC_4H_{10}$						
0.000	14.6487	115.	-0.01	-0.01		-0.02
0.000	14.5521	120.	0.02	0.02		-0.00

Propane Isobutane Mixtures

$0.49030\ C_3H_8 + 0.50970\ iC_4H_{10}$

	Experimental			% Deviation		
Pressure atm	Density mol/ℓ	Temperature K	Corresponding States	Hard Sphere	Revised Klosek and McKinley	Cell Model
0.000	14.3080	105.	-0.01	-0.01		-0.02
0.000	14.2136	110.	-0.01	-0.01		-0.03
0.000	14.1219	115.	0.02	0.02		-0.02
0.000	14.0257	120.	0.01	0.01		-0.03
0.000	13.9300	125.	0.00	0.00		-0.03
0.000	13.8342	130.	-0.01	-0.01		-0.02
			$0.50326\ C_3H_8 + 0.49674\ iC_4H_{10}$			
0.000	13.9718	125.	0.01	0.01		-0.02
0.000	13.8737	130.	-0.01	-0.01		-0.02
			Propane Nitrogen Mixtures			
			$0.93260\ C_3H_8 + 0.06740\ N_2$			
6.230	16.8055	100.	0.01	0.04		-0.08
8.680	16.7084	105.	0.18	0.20		0.05
			$0.96206\ C_3H_8 + 0.03794\ N_4$			
4.890	16.4638	105.	0.01	0.02		-0.06
6.620	16.3410	110.	-0.00	0.00		-0.10
			$0.97986\ C_3H_8 + 0.02014\ N_2$			
3.520	16.2131	110.	-0.01	-0.01		-0.07
4.650	16.0931	115.	-0.02	-0.02		-0.10
			Normal Butane Isobutane Mixtures			
			$0.52961\ nC_4H_{10} + 0.47039\ iC_4H_{10}$			
0.000	12.6943	125.	-0.01	-0.01		-0.02
0.000	12.6133	130.	0.01	0.01		-0.01
0.000	12.5271	135.	-0.01	-0.01		-0.04
0.000	12.4447	140.	0.00	0.00		-0.02

Comparison of Models to Rodosevich Data

$0.9478\ CH_4 + 0.0522\ C_2H_6$

Experimental			% Deviation		
Density mol/ℓ	Temperature K	Corresponding States	Hard Sphere	Revised Klosek and McKinley	Cell Model
27.7678	91.09	-0.00	-0.04	0.01	-0.01
27.0621	100.01	-0.02	-0.06	0.01	-0.05
26.4026	108.08	-0.02	-0.06	0.02	-0.06
25.7573	115.60	-0.04	-0.07	0.02	-0.06
$0.8516\ CH_4 + 0.1484\ C_2H_6$					
27.1003	91.01	-0.04	-0.09	-0.00	-0.01
26.4711	100.01	-0.01	-0.05	0.05	-0.01
25.8859	108.02	-0.05	-0.08	0.02	-0.06
25.3620	115.13	-0.02	-0.05	0.07	-0.03
$0.7528\ CH_4 + 0.2472\ C_2H_6$					
26.4131	91.13	-0.01	-0.05	0.03	0.05
25.8398	100.01	-0.05	-0.08	-0.02	-0.03
25.3235	108.01	-0.03	-0.06	0.01	-0.04
$0.7026\ CH_4 + 0.2974\ C_2H_6$					
26.0647	91.00	-0.03	-0.07	-0.01	0.04
25.0144	108.00	-0.09	- .11	-0.06	-0.09
24.5712	115.00	-0.09	- .10	-0.05	-0.10
$0.6909\ CH_4 + 0.3091\ C_2H_6$					
25.9997	91.00	0.03	-0.01	0.05	0.10
25.4466	100.00	-0.04	-0.06	-0.02	-0.01
24.9476	108.00	-0.08	-0.10	-0.05	-0.08
24.5104	115.00	-0.07	-0.09	-0.04	-0.09
$0.9737\ CH_4 + 0.0263\ C_3H_8$					
27.6870	90.99	-0.01	-0.02	-0.03	-0.01
26.9709	100.03	-0.01	-0.03	-0.03	-0.04
26.3352	107.87	-0.02	0.00	0.00	-0.02
25.7294	114.99	0.02	-0.00	0.01	-0.01

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Experimental		% Deviation			
Density mol/ℓ	Temperature K	Corresponding States	Hard Sphere	Revised Klosek and McKinley	Cell Model
		$0.9262\ CH_4 + 0.0738\ C_3H_8$			
26.9121	91.01	0.01	0.03	-0.02	0.05
26.2667	100.06	0.02	0.03	-0.01	0.03
25.6819	108.01	0.03	0.03	-0.01	0.02
25.1553	114.97	0.04	0.04	0.01	0.04
		$0.8997\ CH_4 + .1003\ C_3H_8$			
26.4774	91.02	-0.02	0.01	-0.06	0.04
25.8692	100.05	-0.01	0.02	-0.06	0.02
25.3165	108.01	0.01	0.02	-0.06	0.01
24.8207	114.98	0.03	0.04	-0.04	0.03
		$0.9506\ CH_4 + 0.0494\ nC_4H_{10}$			
26.5731	95.00	0.03	0.04	0.00	0.13
26.2075	100.00	0.01	0.01	-0.01	0.06
25.6121	108.00	-0.01	-0.02	-0.03	-0.03
25.0771	115.00	-0.02	-0.04	-0.03	-0.09
		$0.9206\ CH_4 + 0.0794\ nC_4H_{10}$			
25.3126	103.00	-0.00	0.02	-0.07	0.09
24.9776	108.00	0.01	0.02	-0.06	0.04
24.4906	115.00	0.00	-0.01	-0.07	-0.05
		$0.9462\ CH_4 + 0.0538\ iC_4H_{10}$			
25.4233	108.00	-0.00	-0.01	-0.21	0.17
26.0010	100.00	-0.03	-0.01	-0.22	0.10
24.8843	115.00	-0.04	-0.08	-0.26	0.18
		$0.9152\ CH_4 + 0.0848\ iC_4H_{10}$			
25.5931	95.00	0.03	0.09	-0.23	0.20
25.2653	100.00	0.03	0.07	-0.26	0.21
24.7274	108.00	0.02	0.02	-0.30	0.25
24.2436	115.00	0.01	-0.04	-0.34	0.30

$0.8466\ CH_4 + 0.1025\ C_2H_6 + 0.0509\ C_3H_8$

Experimental		% Deviation			
Density mol/ℓ	Temperature K	Corresponding States	Hard Sphere	Revised Klosek and McKinley	Cell Model
25.9821	100.01	-0.02	-0.03	-0.03	-0.00
25.4311	108.01	-0.02	-0.03	-0.03	-0.02
25.4278	108.02	-0.03	-0.04	-0.04	-0.03
24.9401	115.00	-0.01	-0.01	-0.01	-0.01
$0.8679\ CH_4 + 0.0818\ C_3H_8 + 0.0503\ iC_4H_{10}$					
24.9240	100.00	-0.01	0.04	-0.19	0.12
24.4194	108.00	-0.02	0.00	-0.22	0.12
23.9670	115.00	-0.02	-0.03	-0.25	0.14
$0.8409\ CH_4 + 0.1086\ C_2H_6 + 0.0505\ N_2$					
27.3493	91.00	-0.06	-0.03	0.10	0.07
25.4706	115.00	-0.06	-0.11	0.03	0.01
26.0417	108.00	-0.04	-0.07	0.02	0.02
26.6667	100.00	-0.05	-0.06	0.10	0.03
$0.9055\ CH_4 + 0.0497\ C_3H_8 + 0.0447\ N_2$					
27.2725	91.00	-0.03	0.03	0.03	0.09
25.9410	108.00	-0.01	-0.01	-0.09	0.06
$0.8303\ CH_4 + 0.1001\ C_2H_6 + 0.0493\ C_3H_8 + 0.0203\ nC_4H_{10}$					
25.5434	100.00	-0.02	-0.00	-0.05	0.03
25.0313	108.00	0.02	0.03	-0.01	0.03
24.5507	115.00	-0.03	-0.02	-0.06	-0.04
$0.9488\ CH_4 + 0.0512\ N_2$					
28.0702	91.00	-0.03	0.01	-0.08	0.02
27.2896	99.99	-0.03	-0.02	-0.04	-0.02
26.5717	108.01	0.01	-0.02	-0.03	-0.02
25.9282	114.98	0.06	0.01	-0.12	0.02

$0.8449\ CH_4 + 0.1551\ nC_4H_{10}$

Experimental			% Deviation		
Density mol/ℓ	Temperature K	Corresponding States	Hard Sphere	Revised Klosek and McKinley	Cell Model
27.9666	91.058	-0.02	0.12		0.16
27.0973	100.35	-0.01	0.04		0.06
26.3387	108.13	-0.00	-0.03		0.01
25.6469	115.05	0.06	0.04		0.03

Comparison of Models for Typical LNG Compositions. Corresponding States Model Was Taken as a Reference

$$0.92834\ CH_4 + 0.04026\ C_2H_6 + 0.00432\ C_3H_8 + 0.00396\ iC_4H_{10} + 0.01813\ N_2$$

Density from Corresponding States Method, mol/ℓ	Temperature K	% Difference Hard Sphere	 Revised Klosek and McKinley	 Cell Model
27.2677	95	0.00	0.03	0.03
26.8737	100	-0.01	0.04	0.02
26.4716	105	-0.02	0.02	0.01

$$0.92779\ CH_4 + 0.03115\ C_2H_6 + 0.02069\ C_3H_8 + 0.02037\ N_2$$

26.4540	105	-0.01	0.03	0.01
26.8562	100	-0.00	0.04	0.01
27.2504	95	0.01	0.04	0.03

$$0.935\ CH_4 + 0.041\ C_2H_6 + 0.009\ C_3H_8 + 0.0025\ nC_4H_{10} + 0.0025\ iC_4H_{10} + 0.01\ N_2$$

27.252	95	-0.01	0.02	0.02
26.8616	100	-0.02	0.03	0.00
26.4632	105	-0.02	0.02	-0.00

$$0.887\ CH_4 + 0.056\ C_2H_6 + 0.024\ C_3H_8 + 0.013\ nC_4H_{10} + 0.013\ iC_4H_{10} + 0.007\ N_2$$

25.6800	105	0.01	-0.04	0.05
26.0342	100	0.02	-0.03	0.06
26.3821	95	0.03	-0.03	0.08

$$0.6975\ CH_4 + 0.156\ C_2H_6 + 0.092\ C_3H_8 + 0.029\ nC_4H_{10} + 0.014\ iC_4H_{10} + 0.0115\ N_2$$

24.3315	95	0.03	-0.05	0.15
24.0648	100	0.07	-0.05	0.11
23.7942	105	0.07	-0.03	0.08

Appendix B. Program Listing for the Extended Corresponding States Model

The program listing that follows is for the extended corresponding states method described in section 2. To use the program in its present form one must make one of the two possible calls to SUBROUTINE PDMIX(P,D,T,X). The two possible calls are

CALL PDMIX(P,D,T,X)

or

CALL PMIX(P,D,T,X)

When the call to PDMIX(P,D,T,X) is made the input variables are: P (pressure in atmospheres); T (temperature in degrees kelvin); and X which is a matrix of the mole fraction of the components of the mixture in the following order

X(1) = mole fraction of methane
X(2) = mole fraction of ethane
X(3) = mole fraction of propane
X(4) = mole fraction of normal butane
X(5) = mole fraction of isobutane
X(6) = mole fraction of nitrogen
X(7) = mole fraction of normal pentane
X(8) = mole fraction of isopentane

No other components are allowed and if one or more of the above components are absent, a zero should be inserted in the appropriate matrix element. The program then calculates a density and it is returned in the argument list as D (density in moles/liter).

When a call to PMIX(P,D,T,X) is made all of the above are the same except that the roles of P and D are interchanged, i.e., D is an input variable and P is calculated by the program.

The range of the program is 90 to 150 kelvin for the saturated liquid phase of any of the pure components of CH_4, C_2H_6, C_3H_2, nC_4H_{10}, iC_4H_{10}, N_2, nC_4H_{12} or iC_4H_{12} or any mixture of those fluids. The program will extrapolate to higher pressures (higher than saturation pressure) but the user is reminded that such a calculation is an extrapolation and should be used with caution.

```
      SUBROUTINE PDMIX(P,D,T,X)
      FOR A CALL TO PDMIX, P,T AND X ARE INPUT.  P IS IN ATM,T IS IN
      KELVIN AND D IS OUTPUT IN THE UNITS OF MOLES/LITER
      FOR A CALL TO P MIX, D,T AND X ARE INPUT AND P IS OUTPUT, THE
      UNITS ARE THE SAME
      THE X MATRIX MUST CONTAIN THE MOL FRACTION OF THE ALLOWABLE FLUIDS
      IN THE FOLLOWING ORDER, 1=C1,2=C2, 3=C3,4=NC4,5=IC4,6=N2
      PLACE A ZERO IN THE ELEMENTS OF X WHERE THAT PARTICULAR GAS IS NOT
      PRESENT
      DIMENSION ZATA(10,10),ATA(10,10),TC(10),VC(10),ZC(10),AC(10),W(10)
     1,PC(10),CF(9)
      DIMENSION THETA(10,10),TH(10,10),PHI(10,10),PH(10,10),F(10,10),FH
     1(10,10),H(10,10),HH(10,10),VR(10,10),TR(10,10),X(10)
      COMMON/DATA M/ZATA,ATA,TC,VC,W,TCO,VCO,ACO,ZCO,RR,R,OMEGO,AC,ZC,N
     1,PC,CF
      DATA(IE=0)
      D=0.0
      GO TO 4
      ENTRY PMIX
      P=0.0
      IP=1
      GO TO 5
    4 IP=0
    5 CONTINUE
      IF(IE.GT.0)GO TO 6
      IE=1
      CALL DATA CH4
      IBASE=L=1
      CALL MIX DATA(IBASE)
    6 CONTINUE
      DO 1 I=1,N
      F(I,I)=H(I,I)=1.
      THETA(I,I)=1.
    1 PHI(I,I)=1.
      DO 30 J=1,30
      HX=FXHX=0.0
      DO 10 I=1,N
      FH(I,I)=F(I,I)
      HH(I,I)=H(I,I)
      IF(X(I).LT..0001)GO T O 10
      F(I,I)=(TC(I)/TC(L))*THETA(I,I)
      H(I,I)=(VC(I)/VC(L))*PHI(I,I)
   10 CONTINUE
      DO 11 IA=1,N
      DO 11 IB=1,N
      IF(X(IA).LT..0001)GO TO 11
      IF(X(IB).LT..0001)GO TO 11
      FAB=ZATA(IA,IB)*(F(IA,IA)* F(IB,IB))**.5
      HAB=ATA(IA,IB)*(.5*H(IA,IA)**(1./3.)+.5*H(IB,IB)**(1./3.))**3
      HX=HX+X(IA)*X(IB)*HAB
      FXHX=FXHX+X(IA)*X(IB)*HAB*FAB
   11 CONTINUE
      FX=FXHX/HX
      PRO=P*HX/FX
      TRO=T/FX
      DEN=D*HX
      IF(IP.EQ.1)GO TO 8
      DD=SATL(TRO)*1000.+1.
    9 DEN=FIND M(PRO,TRO,DD)
    8 CONTINUE
      IF(DEN.LE.0.0) GO TO 33
      VRO=1000./DEN
      DO 12 I=1,N
      IF(X(I).LT..0001)GO TO 12
      VR(I,I)=VRO*PHI(I,I)/VCO
      TR(I,I)=TRO*THETA(I,I)/TCO
      IF(VR(I,I).GT.2.)VR(I,I)=2.
      IF(VR(I,I).LT..5)VR(I,I)=.5
      TH(I,I)=THETA(I,I)
      THETA(I,I)=1.+(AC(I)-OMEGO)*(CF(1)-CF(2)*ALOG(TR(I,I))+(CF(3)-CF(4
     1)/TR(I,I))*(VR(I,I)-CF(5)))
      PH(I,I)=PHI(I,I)
      PHI(I,I)=(1.+(AC(I)-OMEGO)*(CF(6)*(VR(I,I)-CF(7))-CF(8)*(VR(I,I)
     1-CF(9))*ALOG(TR(I,I))))*ZCO/ZC(I)
   12 CONTINUE
      DO 13 I=1,N
      IF(X(I).LT..0001)GO TO 13
      IF(ABS ((FH(I,I)-F(I,I))/F(I,I)).GT..001)GO TO 30
      IF(ABS ((HH(I,I)-H(I,I))/H(I,I)).GT..001)GO TO 30
      IF(ABS ((TH(I,I)-THETA(I,I))/THETA(I,I)).GT..001)GO TO 30
      IF(ABS ((PH(I,I)-PHI(I,I))/PHI(I,I)).GT..001)GO TO 30
   13 CONTINUE
      GO TO 31
   30 CONTINUE
   33 PRINT 100,P,DEN,T
  100 FORMAT(*  ITERATION FAILED AT*,3F10.4)
      STOP
   31 D=DEN/HX
      THC=THETA(6,6)
      IF(IP.EQ.0)GO TO 32
      CALL PRESS(P,DEN,TRO)
      P=P*FX/HX
   32 RETURN
      END
```

```
      SUBROUTINE MIX DATA(IBASE)
      DIMENSION ZATA(10,10),ATA(10,10),TC(10),VC(10),ZC(10),AC(10),W(10)
     1,PC(10),CF(9)
      COMMON/DATA M/ZATA,ATA,TC,VC,W,TCO,VCO,ACO,ZCO,RR,R,OMEGO,AC,ZC,N
     1,PC,CF
      DATA(PC=45.356,47.96757,41.89008,37.79462,36.40758,33.10393)
      DATA(TC=190.555,305.5,370.,425.,408.1,126.2)
      DATA(W=16.04303,30.07012,44.09721,58.1243,58.1243,28.0134)
      DATA(VC=98.522,146.2,200.,251.62,263.00,89.827)
      DATA(AC=.0109,.110427,.154837,.176372,.150115,.0291791)
      DATA(R=82.05606),(RR=8.3144),(N=6)
      DATA(CF=-.109495,.919454,-4.01525,-4.14192,.444850,.356808,
     11.02619,.893323,.761533)
      DATA(ATA(1,2)=1.00514),(ATA(1,3)=1.01922),(ATA(1,4)=1.04454),
     1(ATA(1,5)=1.04931),(ATA(1,6)=1.01009),
     A(ATA(2,3)=1.00599),(ATA(2,4)=1.01616),
     2(ATA(2,5)=1.02369),(ATA(2,6)=1.02127),(ATA(3,4)=1.00172),
     3(ATA(3,5)=1.01140),(ATA(3,6)=1.04606),(ATA(4,5)=.997114),
     4(ATA(4,6)=1.13889),(ATA(5,6)=1.13889)
      DATA(ZATA(1,2)=1.01127),(ZATA(1,3)=.988608),(ZATA(1,4)=.987281),
     1(ZATA(1,5)=.979315),(ZATA(1,6)=.953430),(ZATA(2,3)=.999951),
     2(ZATA(2,4)=.972223),(ZATA(2,5)=.998886),(ZATA(2,6)=.939622),
     3(ZATA(3,4)=.985547),(ZATA(3,5)=1.03099),(ZATA(3,6)=.912209),
     4(ZATA(4,5)=.976416),(ZATA(4,6)= .857310),(ZATA(5,6)=.857310)
      L=IBASE
      N=8
      NI=N-1
      PC(7)=33.37
      PC(8)=31.57
      TC(7)=469.6
      TC(8)=460.39
      VC(7)=304.
      VC(8)=306.
      W(7)=72.15139
      W(8)=72.15139
      AC(7)=.234320
      AC(8)=.288886
      ATA(1,7)=ATA(1,8)=1.04
      ATA(2,7)=ATA(2,8)=1.02
      ATA(3,7)=ATA(3,8)=1.01
      ATA(4,7)=ATA(4,8)=1.
      ATA(5,7)=ATA(5,8)=1.
      ATA(6,7)=ATA(6,8)=1.
      ATA(7,8)=1.
      ZATA(1,7)=ZATA(1,8)=.95
      ZATA(2,7)=ZATA(2,8)=.99
      ZATA(3,7)=ZATA(3,8)=.99
      ZATA(4,7)=ZATA(4,8)=.99
      ZATA(5,7)=ZATA(5,8)=.99
      ZATA(6,7)=ZATA(6,8)=.99
      ZATA(7,8)=1.
      DO 3 J=1,N1
      J1=J+1
      DO 3 K=J1,N
      ZATA(K,J)=ZATA(J,K)
    3 ATA(K,J)=ATA(J,K)
      DO 4 I=1,N
    4 ATA(I,I)=ZATA(I,I)=1.
      PCO=PC(L)
      VCO=VC(L)
      TCO=TC(L)
      OMEGO=AC(L)
      ZCO=PCO*VCO/TCO/R
      DO 5 I=1,N
    5 ZC(I)=PC(I)*VC(I)/TC(I)/R
      RETURN
      END
      SUBROUTINE PROPS(PP,DD,TT)
      DIMENSION X(33)
      DIMENSION B(33),G(32)
      EQUIVALENCE (B,X)
      COMMON/DATA/G,R,GAMMA
      DATA(ID=1)
      DATA(IZ=1)
    1 CONTINUE
      D=DD
      P=PP
      T=TT
      GM=GAMMA
      D2=D*D
      D3=D2*D
      D4=D3*D
      D5=D4*D
      D6=D5*D
      D7=D6*D
      D8=D7*D
      D9=D8*D
      D10=D9*D
      D11=D10*D
      D12=D11*D
      D13=D12*D
      TS=SQRT (T)
      T2=T*T
      T3=T2*T
      T4=T3*T
      T5=T4*T
      F=EXP (GM*D2)
      GO TO (100,200),K
      ENTRY PRESS
      K=1
      GO TO 1
  100 CONTINUE
      B( 1)=D2*T
      B( 2)=D2*TS
      B( 3)=D2
      B( 4)=D2/T
      B( 5)=D2/T2
      B( 6)=D3*T
      B( 7)=D3
      B( 8)=D3/T
      B( 9)=D3/T2
      B(10)=D4*T
      B(11)=D4
      B(12)=D4/T
      B(13)=D5
      B(14)=D6/T
      B(15)=D6/T2
      B(16)=D7/T
      B(17)=D8/T
      B(18)=D8/T2
      B(19)=D9/T2
      B(20)=D3*F/T2
      B(21)=D3*F/T3
      B(22)=D5*F/T2
      B(23)=D5*F/T4
      B(24)=D7*F/T2
      B(25)=D7*F/T3
      B(26)=D9*F/T2
      B(27)=D9*F/T4
      B(28)=D11*F/T2
      B(29)=D11*F/T3
      B(30)=D13*F/T2
      B(31)=D13*F/T3
      B(32)=D13*F/T4
  102 P=0
      DO 101 I=1,32
  101 P=P+B(I)*G(I)
      P=P+R*D*T
      PP=P
      RETURN
      ENTRY DPDD
      K=2
      GO TO 1
  200 CONTINUE
      F1=2.00*F*GM*D
      F21=3.000*F*D2 +F1*D3
      F22=5.000*F*D4 +F1*D5
      F23=7.000*F*D6 +F1*D7
      F24=9.000*F*D8 +F1*D9
      F25=11.00*F*D10+F1*D11
      F26=13.00*F*D12+F1*D13
      B( 1)=2.00*D*T
      B( 2)=2.00*D*TS
      B( 3)=2.00*D
      B( 4)=2.00*D/T
      B( 5)=2.00*D/T2
      B( 6)=3.00*D2*T
      B( 7)=3.00*D2
      B( 8)=3.00*D2/T
      B( 9)=3.00*D2/T2
      B(10)=4.00*D3*T
      B(11)=4.00*D3
      B(12)=4.00*D3/T
      B(13)=5.00*D4
      B(14)=6.00*D5/T
      B(15)=6.00*D5/T2
      B(16)=7.00*D6/T
      B(17)=8.00*D7/T
      B(18)=8.00*D7/T2
      B(19)=9.00*D8/T2
      B(20)=F21/T2
      B(21)=F21/T3
      B(22)=F22/T2
      B(23)=F22/T4
      B(24)=F23/T2
      B(25)=F23/T3
      B(26)=F24/T2
      B(27)=F24/T4
      B(28)=F25/T2
      B(29)=F25/T3
      B(30)=F26/T2
      B(31)=F26/T3
      B(32)=F26/T4
  202 P=0
      DO 201 I=1,32
  201 P=P+B(I)*G(I)
      P=P+R*T
      PP=P
      RETURN
      END
```

```
      SUBROUTINE DATA CH4
      DIMENSION G(32),VP(9),GI(11)
      COMMON/DATA/G,R,GAMMA,VP,DTP
      DIMENSION A(10)
      COMMON/SATC/A
      R=.08205616
      GAMMA=-.0096
      A(1)=190.555
      A(2)=10.23
      A(3)=18.404156472
      A(4)=7.3498921512
      A(5)=-1.4313160833
      A(6)=A(7)=0.0
      G( 1)=-.187027997685E-01
      G( 2)= .103387138009E+01
      G( 3)=-.155387625619E+02
      G( 4)= .772311478564E+03
      G( 5)=-.377103300895E+05
      G( 6)= .846818843475E-03
      G( 7)=-.496415884529E+00
      G( 8)= .869909352414E+02
      G( 9)=-.322821592493E+05
      G(10)=-.395843026316E-04
      G(11)= .266772318035E-01
      G(12)=-.304010057839E+01
      G(13)= .191584507536E-03
      G(14)=-.195587933458E-03
      G(15)= .607479967879E+01
      G(16)=-.529609525984E-03
      G(17)= .152264286004E-04
      G(18)=-.109952182842E-01
      G(19)= .191395549929E-03
      G(20)= .386470003746E+05
      G(21)=-.157930582612E+07
      G(22)= .195270144401E+03
      G(23)= .165996081629E+07
      G(24)= .603051146711E+00
      G(25)= .376485162808E+02
      G(26)= .125593680622E-02
      G(27)=-.343570032513E+02
      G(28)=-.540945094139E-05
      G(29)= .185622284663E-02
      G(30)= .770786979245E-08
      G(31)=-.286668318650E-05
      G(32)= .372376961647E-04
      END
      FUNCTION SATL(T)
      DIMENSION A(10)
      COMMON/SATC/A
      IF(T.GT.A(1))GO TO 1
      X=(1.-T/A(1))
      SATL=A(2)+A(3)*X**(.35)+A(4)*X+A(5)*X**(4./3.)+A(6)*X**(5./3.
     1)+A(7)*X**2
      SATL=SATL/1000.
      RETURN
    1 SATL=1.E20
      RETURN
      END
```

```
      FUNCTION FIND M(P,T,D)
      DD=D
      TT=T
      DO 10 I=1,50
      CALL PRESS(PP,DD,TT)
      P2=PP
      IF(ABS (P-P2)-1.E-7*P) 20,20,1
    1 CALL DPDD(PP,DD,TT)
      DP=PP
      CORR=(P2-P)/DP
      IF(ABS (CORR)-1.E-7*DD) 20,20,10
   10 DD=DD-CORR
      FIND M=0
      RETURN
   20 FIND M=DD
      RETURN
      END
```

Appendix C. Program Listing for the Hard Sphere Model

The program listing that follows is for the hard sphere model described in section 3. To use the program in its present form one must make the following reference to the computer program

DEN = RODEN(P,T,X)

where DEN is density in moles/liter, P is pressure in atmospheres, T is temperature in degrees kelvin, and X is a matrix of the mole fractions of the components of the mixture in the following order

X(1) = mole fraction of methane
X(2) = mole fraction of ethane
X(3) = mole fraction of propane
X(4) = mole fraction of normal butane
X(5) = mole fraction of isobutane
X(6) = mole fraction of nitrogen
X(7) = mole fraction of isopentane
X(8) = mole fraction of methylpentane

Note: The inclusion of the pentanes is due to Rodosevich and Miller (1975) and no checking or optimization of parameter has been included in this work for mixtures with pentane as a component.

The range of the program is 90 to 150 kelvin for the saturated liquid phase of mixtures of CH_4, C_2H_6, C_3H_8, iC_4H_{10}, nC_4H_{10} and N_2. The program will calculate densities of any of the pure components but they will be from a different model (i.e., some from an equation of state (CH_4 and N_2) and some from the equations for saturated liquid densities. Therefore in its present form, extrapolation to higher pressures is possible but the reliability of the results is questionable.

```
      FUNCTION RODEN(P,T,X)
      DIMENSION X(10)
      CALL FM(P,T,X,V,G)
      D=28.
      V=V+V IDEL(P,C,T,X)
      RODEN=1000./V
      RETURN
      END
      SUBROUTINE FM(Q,T,X,V9,G9)
      PREDICTION OF EXCESS PROPERTIES WITH LHW XOTENTIAL, COMP 1-METH
      ANE,COMP 2-ETHANE,COMP 3-PROPANE,COMP 4 N-BUTANE,COMP 5-I-BUT
      ANE, COMP 6-NITROGEN, COMP G-ISOPENTANE,COMP 8-METHYLPENTANE
      ADV CRYO ENGR. VOL. I9 (1973)-REPROGRAMED BY R. MCCARTY,2/22/74
      ARGUMENTS ARE X-MOLE FRACTIONS,T-TEMPERATURE,Q-PRESSURE,V9-EXCESS
      VOLUME,G9-EXCESS GIBBS ENERGY, FIRST THREE ARE9INPUT,LAST TWO ARE
      OUTPUT,INPUT IS IN KELVINS AND ATM,
      DIMENSION A(8),B(8)      ,S(8),V(8),G(8),C(8,8),D(8,8),K(3,8),
     1J(8,8),E(8),Y(8),O(8),X(10)
      TYPE REAL J,K,N1
      DATA(KEY=1)
      DATA(J(1,2)=-.00388616),(J(1,3)=-.0120932),(J(1,4)=-.0180737),
     A(J(1,5)=-.0181962),(J(1,6)=-.00997547),(J(1,7)=-.0326),(J(1,8)=
     B-.0458),(J(2,4)=-.00400910),(J(2,5)=-.00812712),(J(2,6)=-.0143976)
     C,(J(2,7)=-.003),(J(2,8)=-.004),(J(3,4)=+.0007615710),(J(3,5)=-.003
     D83743),(J(3,6)=-.024014),(J(3,7)=0.0),(J(3,8)=0.0),(J(4,5)=.002221
     E50),(J(4,7)=.0),(J(4,8)=.0),(J(5,6)=-.0576043),(J(4,6)=-.0576043),
     F(J(5,7)=.0),(J(5,8)=0.0),(J(6,7)=-.04),(J(6,8)=-.05),(J(7,8)=.0)
     G ,(J(2,3)=-.002162)
      DATA(K(1,2)=.00298830),(K(1,3)=.0597378),(K(1,4)=.1189470),(
     AK(1,5)=.116009),(K(1,6)=.0197290),(K(1,7)=.14),(K(1,8)=.1745),
     B(K(2,4)=.0677703),(K(2,5)=.0346632),(K(2,6)=.0529034),(K(2,7)=
     C.02),(K(2,8)=.03),(K(3,4)=.0249291),(K(3,5)=-.00838212),(K(4,5)=.0
     D199213),(K(4,6)=.154365 ),(K(4,7)=.0),(K(4,8)=.0),(K(5,6)=.154365)
     E,(K(5,7)=.0),(K(5,8)=.0),(K(6,7)=.15),(K(6,8)=.18),(K(7,3)=0.0)
     F,(K(2,3)=.014527),(K(3,6)=.14719),(K(3,7)=0.0),(K(3,8)=0.0)
      DATA(S=3.676E-8,4.158E-8,4.644E-8,5.051E-8,5.056E-8,3.545E-8,
     15.389E-8,5.706E-8)
      DATA(A=2.755E+5,7.773E+5,14.165E+5,22.733E+5,21.279E+5,1.718E+5,
     130.550E+5,42.946E+5)
      DATA(O=1.,1.5,1.67,1.83,1.79,1.03,1.91,2.11)
      THESE ARE THE ACENTRICITY FACTORS (FOR MOLECULAR SHAPES,ETC.)   *****
      DATA(Y=35.,45.,60.,75.,75.,40.,90.,105.)
      DATA(PI=3.14159),(NI=6.025E+23),(R=8.3143   )
      IF(KEY.EQ.0)GO TO 1
      KEY=0
      DO 2 I=1,8
      J(I,I)=0.0
      K(I,I)=0.0
      DO 2 M=I,8
      J(M,I)=J(I,M)
    2 K(M,I)=K(I,M)
    1 CONTINUE
      P=Q*.101325
      IW=8
      DO 10 I=1,IW
   10 E(I)=O(I)
      DO 15 I=1,IW
   15 B(I)=(2./3.)*P1*N1*S(I)**3
      DO 20 I=1,IW
      DO 20 M=1,IW
      D(I,M) =(((B(I)**( 1./3. ) + B(M) ** ( 1./3.))/ 2. )*(1.-J(I,M) ))
     1 **3
   20 C( I , M ) = ( 1. - K( I, M ) ) * ( A(I)* A(M) ) ** ( 1. / 2. ) *
     1( D( I, M ) **2 / ( B(I) * B(M) ) ) ** ( 1./2. )
```

```
      A2=0  $  B2=0
      E2=0  $  V2=0
      DO 25 I=1,IW
      V2=V2+X(I)*Y(I)
      DO 25 M=1,IW
      E2=E2+X(I)*X(M)*(E(I)+E(M))/2.
      A2 = A2    + X(I)  * X(M)  * C( I, M )
   25 B2=B2+X(I)*X(M)*D(I,M)
      V6=V2
      DO 30 I = 1, IW
      A3 = A(I)
      B3 = B(I)
      E3 = E(I)
      V2 = Y(I)
      V1 = FIND V1( A3, B3, E3, R, V2, P, T)
      G1 = FIND G1( A3, B3, E3, R, V2, P, T)
      V(I) = V1
   30 G(I) = G1
      A3=A2
      B3=B2
      E3=E2
      V2=V6
      V1=FIND V1(A3,B3,E3,R,V2,P,T)
      G1=FIND G1(A3,B3,E3,R,V2,P,T)
      V7=V1
      G7=G1
      EXCEAS VOLUME AND GIBS ENERGY
      V9=0
      G9=0
      DO 35 I=1,IW
      V9=V9-X(I)*V(I)
   35 G9=G9-X(I)*G(I)
      W9 = -V9
      H9 = -G9
      V9=V9+V7
      G9=G9+G7
      VIWW=V(IWW)
      RETURN
      END
      FUNCTION FIND V1( A3, B3, E3,R, V2, P, T )
      A2 IS THE CONSTANT A, B2 IS THE CONSTANT B, E3 IS THE ACENTRICITY FACTOR.
      INDEX = 0
    1 V1 = V2
      X1 = B3 / ( 4. * V1 )
      F2 = (( 1. + X1 + X1**2) / ( 1. - X1)**3) * E3 -A3 / ( V1 * R * T)
     1- (P * V1) / ( R*T)
      F3 = A3 / (R*T*V1**2) - P/ (R*T)
      F3 = F3 - ((( X1 + 2.* X1**2) * ( 1 - X1) + 3* ( 1. + X1 + X1**2)
     1* X1) / (( 1. - X1 )**4 * V1)) * E3
      V2 = V1 - F2/ F3
      IF( ABS( (V2 - V1) / V2) .LT. .00001 )   GO TO 2
      INDEX = INDEX + 1
      IF( INDEX .LT. 250 ) GO TO 1
      FLAG = ABS( (V2 - V1 ) / V2 )
    5 FORMAT(28H0 ABS( (V2 - V1) / V2 )  =      1F10.5 )
    2 V1 = V2
      FIND V1 = V2
      RETURN
      END
      FUNCTION FIND G1( A3, B3, E3,R, V2, P, T )
      V1 = V2
      X1 = B3 / ( 4. * V1 )
      G1 =ALOG( 1. / ( 1. - X1 )) +(3. *X1) / ( 1. - X1) + ( 3. * X1**2)
     1 / (2. * ( 1. - X1 )**2)
      G1 = G1 - A3 / ( E3 * R * T*V1 ) + ( P * V1) / ( E3 * R * T ) -1.0
     1 - ALOG( V1 )
      G1 = R * T * E3 * G1
      FIND G1 = G1
      RETURN
      END

      FUNCTION EXCESS(P,DD,T,X)
      DIMENSION X(10),F(10)
      KR=0
      GO TO 1
      ENTRY V IDEL
      KR=1
    1 CONTINUE
      CALL ZERO(F)
      IF(X(1).LE..000001)GO TO 2
      CALL DATA CH4
      IF(T.GT.190.555)GO TO 12
      PM=VPN(T)+.00001
      DELP=P-PM
      D=SAT(T,1)
      CALL DPDD(DP,D,T)
      DELD=DELP/DP
      D=DELD+D
      F(1)=X(1)*1000./D
      GO TO 2
   12 D=FIND M(P,T,DD)
      IF(D.LE.0.0)D=1000.
      F(1)=X(1)*1000./D
    2 IF(X(2).LE. .000001)GO TO 3
      F(2)=X(2)*1000./SAT(T,2)
    3 IF(X(3).LE..000001)GO TO 4
      F(3)=X(3)*1000./SAT(T,3)
    4 IF(X(4).LE..00001)GO TO 5
      F(4)=X(4)*1000./SAT(T,4)
    5 IF(X(5).LE..00001)GO TO 6
      F(5)=X(5)*1000./SAT(T,5)
    6 IF(X(6).LE..00001)GO TO 8
      CALL DATA N2
      IF(T.GT.126.6)GO TO 7
      PN=VPN(T)+.000001
      DELP=P-PN
      D=SAT(T,6)
      CALL DPDD(DP,D,T)
      F(6)=X(6)*1000./(D+DELP/DP)
      GO TO 8
    7 D=FIND M(P,T,DD)
      IF(D.LE.0.0)D=1000.
      F(6)=X(6)*1000./D
    8 V=1000./DD
      VS=0
      DO 21 I=1,6
   21 VS=VS+F(I)
      EXCESS=V-VS
      IF(KR.GT.0)EXCESS=VS
      CALL DATA CH4
      RETURN
      END
      SUBROUTINE DATA 42
      COMMON/DATA/G,R,GAMMA,VP,DTP
      DIMENSION G(32),VP(9)
      R=8.20539D-2
      GAMMA=-.0056
      G( 1)=     0.136224769272827E-02
      G( 2)=     0.107032469908591E 00
      G( 3)=    -0.243901721871413E 01
      G( 4)=    -0.341397449376470E 02
      G( 5)=    -0.422374309466167E 04
      G( 6)=     0.155390600246494E-03
      G( 7)=    -0.112594826522081E-01
      G( 8)=     0.142600739270007E-07
      G( 9)=     0.184698501609007E 05
      G(10)=     0.611140682583776E-07
      G(11)=     0.233011645038006E-02
      G(12)=    -0.527752536353986E 00
      G(13)=     0.485027881931214E-04
      G(14)=    -0.113550764115364E-02
      G(15)=    -0.707430273540575E 00
      G(16)=     0.751796548352600E-04
      G(17)=    -0.111614119537424E-05
      G(18)=    -0.358796562237495E-03
      G(19)=    -0.201317691347729E-05
      G(20)=    -0.159717444759949E 05
      G(21)=    -0.119719240044192E 06
      G(22)=    -0.375210272030201E 02
      G(23)=     0.554639713151823E 05
      G(24)=    -0.179920450447470E 00
      G(25)=    -0.256582926077184E 01
      G(26)=    -0.413707715099779E-03
      G(27)=    -0.256245415300293E 00
      G(28)=    -0.124222373740063E-06
      G(29)=     0.103556535840165E-04
      G(30)=    -0.533669215685330E-09
      G(31)=    -0.757415412839596E-08
      G(32)=     0.545336717706952E-07
      VP(1)=5.1113192394 $ VP(2)=6.482667539E-1
      VP(3)=-1.51037309151E-1 $ VP(4)=7.41284933425E-1
      VP(5)=1.5 $ VP(6)=.123 $ VP(7)=63.15 $ VP(8)=126.25
      VP(9)=0.0
      DTP=31.0
      RETURN $ END
      SUBROUTINE DATA CH4
      DIMENSION G(32),VP(9)
      COMMON/DATA/G,R.GAMMA,VP,DTP
      R=.08205616
      GAMMA=-.0096
      G( 1)= -.[illegible]
      G( 2)=  .107387106009E+01
      G( 3)= -.[illegible]
      G( 4)=  .772311473564E+03
      G( 5)= -.[illegible]
      G( 6)=  .346813343475E-03
      G( 7)= -.[illegible]
      G( 8)=  .369909352414E+02
      G( 9)= -.[illegible]
      G(10)= -.795843026318E-04
      G(11)=  .[illegible]
      G(12)= -.304010057339E+01
      G(13)=  .[illegible]
      G(14)= -.135587933458E-03
      G(15)=  .[illegible]
      G(16)= -.529603525984E-03
      G(17)=  .[illegible]
      G(18)= -.109952132842E-01
      G(19)=  .[illegible]
      G(20)=  .336470003746E+05
      G(21)= -.[illegible]
      G(22)=  .195270144401E+03
      G(23)=  .[illegible]
      G(24)=  .633051146711E+00
      G(25)=  .[illegible]
      G(26)=  .1255936580622E-02
      G(27)= -.[illegible]
      G(28)= -.540945394139E-05
      G(29)=  .[illegible]
      G(30)=  .7707356979245E-08
      G(31)= -.[illegible]
      G(32)=  .372376351647E-14
      VP(1)=[illegible]
      VP(2)=1.76065363
      VP(3)=-.[illegible]
      VP(4)=1.32786231
      VP(5)=1.5
      VP(6)=.1158993
      VP(7)=[illegible]
      VP(8)=190.555
      VP(9)=[illegible]
      RETURN
      END
      FUNCTION [illegible](P,T,D)
      DD=D
      TT=T
      DO 10 I=1,50
      CALL PRESS(PP,DD,TT)
      P2=PP
      IF(ABS (P-P2)-1.E-7*P)21,21,1
    1 CALL DPDD(PP,DD,TT)
      DP=PP
      CORR=(P2-P)/DP
      IF(ABS (CORR)-1.E-7*DD)21,21,10
   10 DD=DD-CORR
      [illegible]
      RETURN
```

```
 33 FIND M=33
    RETURN
    END



    SUBROUTINE PROPS(PP,DD,TT)
    DIMENSION X(33)
    DIMENSION B(33),G(32)
    EQUIVALENCE (B,X)
    COMMON/DATA/G,R,GAMMA
  1 CONTINUE
    D=DD
    P=PP
    T=TT
    GM=GAMMA
    D2=D*D
    D3=D2*D
    D4=D3*D
    D5=D4*D
    D6=D5*D
    D7=D6*D
    D8=D7*D
    D9=D8*D
    D10=D9*D
    D11=D10*D
    D12=D11*D
    D13=D12*D
    TS=SQRT (T)
    T2=T*T
    T3=T2*T
    T4=T3*T
    T5=T4*T
    F=EXP (GM*D2)
    GO TO (100,200),K
    ENTRY PRESS
    K=1
    GO TO 1
100 CONTINUE
    B( 1)=D2*T
    B( 2)=D2*TS
    B( 3)=D2
    B( 4)=D2/T
    B( 5)=D2/T2
    B( 6)=D3*T
    B( 7)=D3
    B( 8)=D3/T
    B( 9)=D3/T2
    B(10)=D4*T
    B(11)=D4
    B(12)=D4/T
    B(13)=D5
    B(14)=D6/T
    B(15)=D6/T2
    B(16)=D7/T
    B(17)=D8/T
    B(18)=D8/T2
    B(19)=D9/T2
    B(20)=D3*F/T2
    B(21)=D3*F/T3
    B(22)=D5*F/T2
    B(23)=D5*F/T4
    B(24)=D7*F/T2
```

```
      B(25)=D7*F/T3
      B(26)=D9*F/T2
      B(27)=D9*F/T4
      B(28)=D11*F/T2
      B(29)=D11*F/T3
      B(30)=D13*F/T2
      B(31)=D13*F/T3
      B(32)=D13*F/T4
      P=0
      DO 101 I=1,32
  101 P=P+B(I)*G(I)
      P=P+P*D*T
      PP=P
      RETURN
      ENTRY DPDD
      K=2
      GO TO 1
  200 CONTINUE
      F1=2.D0*F*GM*D
      F21=3.0D0*F*D2 +F1*D3
      F22=5.0D0*F*D4 +F1*D5
      F23=7.0D0*F*D6 +F1*D7
      F24=9.0D0*F*D8 +F1*D9
      F25=11.D0*F*D10+F1*D11
      F26=13.D0*F*D12+F1*D13
      B( 1)=2.D0*D*T
      B( 2)=2.D0*D*TS
      B( 3)=2.D0*D
      B( 4)=2.D0*D/T
      B( 5)=2.D0*D/T2
      B( 6)=3.D0*D2*T
      B( 7)=3.D0*D2
      B( 8)=3.D0*D2/T
      B( 9)=3.D0*D2/T2
      B(10)=4.D0*D3*T
      B(11)=4.D0*D3
      B(12)=4.D0*D3/T
      B(13)=5.D0*D4
      B(14)=6.D0*D5/T
      B(15)=6.D0*D5/T2
      B(16)=7.D0*D6/T
      B(17)=8.D0*D7/T
      B(18)=8.D0*D7/T2
      B(19)=9.D0*D8/T2
      B(20)=F21/T2
      B(21)=F21/T3
      B(22)=F22/T2
      B(23)=F22/T4
      B(24)=F23/T2
      B(25)=F23/T3
      B(26)=F24/T2
      B(27)=F24/T4
      B(28)=F25/T2
      B(29)=F25/T3
      B(30)=F26/T2
      B(31)=F26/T3
      B(32)=F26/T4
      P=0
      DO 201 I=1,32
  201 P=P+R(I)*G(I)
      P=P+R*T
      PP=P
      RETURN
      END
```

```
    FUNCTION SAT(T,I)
    UNITS ARE DEG K AND MOLES/LITER
    DIMENSION A(7,6)
    DATA((A(I).I=1,7)=190.555,10.16,18.65812322,6.712030737,
   1-.3472319712,0.0,0.0)
    DATA((A(I),I=8,14)=305.33,
   1        6.83,12.55205121,13.47294373,-19.08461066,11.37715965,0.0)
    DATA((A(I),I=15,21)=369.82,5.,8.684458671,18.04085714,-29.46261356
   1,16.43559114,0.0)
    DATA((A(I),I=22,28)=425.16,3.92,
   1                                7.285062567,11.96337859,-19.37591962,
   211.60211932,0.0)
    DATA((A(I),I=29,35)=408.13,3.8,
   1                                7.657535400,8.145251283,-13.10582462,
   23.14539121,0.0)
    DATA((A(I),I=36,42)=126.2,11.21,19.39216835,26.01408462,-39.497587
   131.23.32077312,0.0)
    IF(T.GT.A(1,I))GO TO 1
    X=(1.-T/A(1,I))
    SAT=(A(2,I)+A(3,I)*X**(.35)+A(4,I)*X+A(5,I)*X**(4./3.)
   1+A(6,I)*X**(5./3.))
    RETURN
  1 SAT=1.E+20
    RETURN
    END
```

```
    FUNCTION VPN(TT)
    DIMENSION G(32),VP(9)
    COMMON/DATA/G,R,GAMMA,VP,DTP
    T=TT
    X=(1.-VP(7)/T)/(1.-VP(7)/VP(8))
    VPN=VP(6)*EXP(VP(1)*X+VP(2)*X*X+VP(3)*X**3+VP(9)*X**4+VP(4)*X*
   1(1.-X)**VP(5))
    RETURN
  1 VPN=.01
    RETURN
    END
```

```
    SUBROUTINE ZERO(X)
    DIMENSION X(10)
    DO 1 I=1,10
  1 X(I)=0.0
    RETURN
    END
```

Appendix D. Program Listing for the Revised Klosek and McKinley Model

The program listing and tables that follow are for the Revised Klosek and McKinley model described in section 4. The method may be used in two ways. First using the equation

$$V_{mix} = \Sigma X_i V_i - [k_1 + (k_2 - k_1) X_{N_2}/0.0425] X_{CH_4} \qquad (C-1)$$

The V_i, k_1 and k_2 may be obtained from tables 1, 2 and 3 and the volume of the mixture calculated. For example given the mixture of 0.8130 CH_4 + 0.0475 C_2H_6 + 0.0487 C_3H_8 + 0.0242 nC_4H_{10} + 0.0241 iC_4H_{10} + 0.0425 N_2 and a temperature of 105 kelvin.

The $\Sigma X_i V_i$ is obtained from table 1.

$$\Sigma X_i V_i = (.8130)(.037112) + (.0475)(.047266) + (.0487)(.061766) + (.0242)(.076100) + (.0241)(.077538) + (.0425)(.042560)$$

Then the $\Sigma X_i W_i = (.8130)(16.04303) + (.0475)(30.07012) + (.0487)(44.09721) + (.0242)(58.1243) + (.0241)(58.1243) + (.0425)(28.0134)$

= 20.6168 the molecular weight of the mixture

from table 2 $k_1 = .730 \times 10^{-3}$

from table 3 $k_2 = .849 \times 10^{-3}$

plugging all this into equation (C-1) gives

$$V_{mix} = .040944$$

$$1/V_{mix} = \rho_{mix} = 24.858 \text{ moles/liter}$$

This compares to the experimental values of 24.850 (see last page of Appendix E) to within 0.03%.

The same result may be obtained by using the computer program in the following way

```
D = FMKM(T,X)
```

where T is temperature in kelvins and X is a matrix of mole fractions of the components in the following order:

X(1) = mole fraction of methane
X(2) = mole fraction of ethane
X(3) = mole fraction of propane
X(4) = mole fraction of normal butane
X(5) = mole fraction of isobutane
X(6) = mole fraction of nitrogen
X(7) = mole fraction of normal pentane
X(8) = mole fraction of isopentane

for the example: T = 105., X(1) = .8130, X(2) = .0475, X(3) = .0487, X(4) = .0242, X(5) = .0241 and X(6) = .04256.

Table 1. Volumes of Saturated Liquid of the Pure Components in Liters/mole.

T, K	CH_4	C_2H_6	C_3H_8	nC_4H_{10}	iC_4H_{10}	N_2	nC_5H_{12}	iC_5H_{12}
90.	.035441	.046081	.060461	.074708	.076084	.037543	.089173	.089243
92.	.035649	.046235	.060632	.074891	.076274	.038081	.089379	.089454
94.	.035861	.046390	.060804	.075075	.076466	.038650	.089586	.089666
96.	.036077	.046547	.060977	.075259	.076659	.039254	.089793	.089878
98.	.036298	.046704	.061151	.075445	.076853	.039897	.090000	.090091
100.	.036524	.046863	.061325	.075631	.077047	.040586	.090208	.090304
102.	.036755	.047023	.061501	.075818	.077243	.041327	.090416	.090518
104.	.036992	.047185	.061677	.076006	.077440	.042128	.090624	.090733
106.	.037234	.047348	.061855	.076194	.077637	.043002	.090833	.090948
108.	.037481	.047512	.062033	.076384	.077836	.043963	.091042	.091163
110.	.037735	.047678	.062212	.076574	.078035	.045031	.091252	.091379
112.	.037995	.047845	.062392	.076765	.078236	.046231	.091462	.091596
114.	.038262	.048014	.062574	.076957	.078438	.047602	.091673	.091814
116.	.038536	.048184	.062756	.077150	.078640	.049179	.091884	.092032
118.	.038817	.048356	.062939	.077344	.078844	.050885	.092095	.092251
120.	.039106	.048529	.063124	.077539	.079049	.052714	.092307	.092470
122.	.039404	.048704	.063309	.077734	.079255	.054679	.092520	.092690
124.	.039710	.048881	.063496	.077931	.079462	.056797	.092733	.092911
126.	.040025	.049059	.063684	.078128	.079671	.059085	.092947	.093133
128.	.040350	.049239	.063873	.078327	.079880	.061565	.093161	.093355
130.	.040685	.049421	.064063	.078526	.080091	.064263	.093376	.093578
132.	.041031	.049605	.064254	.078727	.080303	.067208	.093591	.093801
134.	.041389	.049790	.064446	.078928	.080516	.070435	.093807	.094026
136.	.041760	.049978	.064640	.079130	.080730	.073989	.094024	.094251
138.	.042144	.050167	.064835	.079334	.080946	.077919	.094241	.094477
140.	.042542	.050359	.065031	.079538	.081162	.082291	.094459	.094704
142.	.042956	.050552	.065229	.079744	.081380	.087183	.094678	.094932
144.	.043387	.050748	.065427	.079950	.081600	.092693	.094897	.095160
146.	.043836	.050946	.065628	.080158	.081821	.098947	.095117	.095389
148.	.044304	.051146	.065829	.080367	.082043	.106105	.095338	.095620
150.	.044794	.051348	.066032	.080577	.082266	.114380	.095560	.095851

Table 2. Correction Factor $k_1 \times 10^3$

T/W	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
90.	-.005	.12	.22	.34	.43	.51	.59	.66	.75	.82	.88	.93	.98	1.03	1.08
95.	-.006	.14	.26	.38	.49	.58	.67	.75	.85	.92	.99	1.05	1.10	1.15	1.20
100.	-.007	.15	.30	.42	.54	.65	.75	.86	.96	1.04	1.11	1.17	1.23	1.28	1.34
105.	-.007	.17	.34	.46	.62	.73	.84	.96	1.08	1.16	1.24	1.31	1.37	1.43	1.49
110.	-.008	.19	.38	.54	.70	.82	.93	1.06	1.21	1.30	1.39	1.47	1.53	1.60	1.67
115.	-.009	.22	.42	.61	.79	.93	1.06	1.20	1.36	1.47	1.56	1.65	1.71	1.79	1.86
120.	-.010	.25	.50	.70	.90	1.04	1.23	1.40	1.54	1.65	1.75	1.85	1.92	2.00	2.08
125.	-.013	.30	.59	.79	1.02	1.18	1.38	1.60	1.73	1.86	1.97	2.08	2.15	2.24	2.33
130.	-.015	.35	.70	.92	1.14	1.36	1.60	1.73	1.96	2.09	2.22	2.34	2.42	2.52	2.62
135.	-.017	.40	.80	1.06	1.39	1.51	1.77	1.90	2.23	2.38	2.52	2.64	2.74	2.85	2.95

Table 3. Correction Factor $k_2 \times 10^3$

T/W	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
90.	-.004	.10	.22	.35	.50	.60	.69	.78	.86	.95	1.03	1.12	1.20	1.27	1.35
95.	-.005	.12	.28	.43	.59	.71	.83	.94	1.05	1.14	1.22	1.28	1.37	1.45	1.54
100.	-.007	.16	.34	.49	.64	.79	.94	1.08	1.17	1.27	1.37	1.47	1.57	1.67	1.77
105.	-.010	.24	.42	.61	.75	.91	1.05	1.19	1.33	1.45	1.58	1.69	1.81	1.92	2.03
110.	-.015	.32	.59	.77	.92	1.07	1.22	1.37	1.52	1.71	1.83	1.97	2.10	2.23	2.36
115.	-.024	.55	.72	.95	1.15	1.22	1.30	1.45	1.65	2.00	2.17	2.32	2.47	2.63	2.79
120.	-.032	.75	.91	1.23	1.43	1.63	1.85	2.08	2.30	2.45	2.60	2.77	2.95	3.13	3.32
125.	-.043	1.00	1.13	1.48	1.73	1.98	2.23	2.48	2.75	2.90	3.10	3.30	3.52	3.74	3.96
130.	-.058	1.34	1.46	1.92	2.20	2.42	2.68	3.00	3.32	3.52	3.71	3.95	4.20	4.46	4.74
135.	-.075	1.75	2.00	2.40	2.60	3.00	3.40	3.77	3.99	4.23	4.47	4.76	5.05	5.36	5.69

```
      FUNCTION FMKM(T,X)
      DIMENSION TM(150),TN(150),X(10),Q(8)
      DATA(Q=16.04303,30.07012,44.09721,58.1243,58.1243,28.0134,72.1513
     19,72.15139)
      DATA((TM(I),I=1,15)=-.005,.A2,.22,.34,.43,.51,.59,.66,.75,.82,
     A.88,.93,.98,1.03,1.08)
      DATA((TM(I),I=16,30)=-.006,,14,.26,.38,.49,.58,.67,.75,.85,.92,
     A.99,1.05,1.1,1.15,1.2)
      DATA((TM(I),I=31,45)=-.007,.15,.3,.42,.54,.65,.75,.86,.95,1.04,
     A1.11,1.17,1.23,1.28,1.34)
      DATA((TM(I),I=46,60)=-.007,,17,.34,.46,.62,.73,.84,.96,1.08,1.16,
     A1.24,1.31,1.37,1.43,1.49)
      DATA((TM(I),I=61,75)=-.008,.19,.38,.54,.7,.82,.93,1.06,1.21,1.3,
     A1.39,1.47,1.53,1.6,1.67)
      DATA((TM(I),I=76,90)=-.009,,22,.42,.61,.79,.93,1.06,1.2,1.36,1.47,
     A1.56,1.65,1.71,1.79,1.86)
      DATA((TM(I),I=91,105)=-.01,.25,.5,.7,.9,1.04,1.23,1.4,1.54,1.65,
     A1.75,1.85,1.92,2.,2.08)
      DATA((TM(I),I=106,120)=-.013,.3,.59,.79,1.02,1.18,1.38,1.6,1.73,
     11.86,
     A1.97,2.08,2.15,2.24,2.33)
      DATA((TM(I),I=121,135)=-.015,.35,.7,.92,1.14,1.36,1.6,1.73,1.96,
     A2.09,2.22,2.34,2.42,2.52,2.62)
      DATA((TM(I),I=136,150)=-.017,.4,.80,1.06,1.39,1.51,1.77,1.9,2.23,2
     A.38,2.52,2.64,2.74,2.85,2.95)
      DATA((TN(I),I=1,15)=-.004,.1,.22,.35,.5,.6,.69,.78,.86,.95,
     A1.03,1.12,1.20,1.27,1.35)
      DATA((TN(I),I=16,30)=-.005,,12,.28,.43,.59,.71,.83,.94,1.05,1.14,
     A1.22,1.28,1.37,1.45,1.54)
      DATA((TN(I),I=31,45)=-.007,,16,.34,.49,.64,.79,.94,1.08,1.17,1.27,
     A1.37,1.47,1.57,1.67,1.77)
      DATA((TN(I),I=46,60)=-.01,.24,.42,.61,.75,.91,1.05,1.19,1.33,1.45,
     A1.58,1.69,1.81,1.92,2.03)
      DATA((TN(I),I=61,75)=-.015,.32,.59,.77,.92,1.07,1.22,1.37,1.52,
     I1.71,
     A1.83,1.97,2.1,2.23,2.36)
      DATA((TN(I),I=76,90)=-.024,,55,.72,.95,1.15,1.22,1.3,1.45,1.65,2.,
     A2.17,2.32,2.47,2.63,2.79)
      DATA((TN(I),I=91,105)=-.032,.75,.91,1.23,1.43,1.63,1.85,2.08,2.3,
     12.45
     A,2.6,2.77,2.95,3.13,3.32)
      DATA((TN(I),I=106,120)=-.043,1.,1.13,1.48,1.73,1.98,2.23,2.48,2.75
     1,
     A2.9,3.1,3.3,3.52,3.74,3.96)
      DATA((TN(I),I=121,135)=-.058,1.34,1.46,1.92,2.2,2.42,2.63,3.,
     A3.32,3.52,3.71,3.95,4.2,4.46,4.74)
      DATA((TN(I),I=136,150)=-.075,1.75,2.,2.4,2.6,3.,3.4,3.77,
     A3.99,4.23,4.47,4.76,5.05,5.36,5.69)
      IF(X(1).LT..00001)GO TO 20
      AW=0.0
      DO 1 I=1,8
    1 AW=AW+X(I)*Q(I)
      VI=VIDEAL(T,X)
      J=1
      IF(T.GE.95.)J=16
      IF(T.GE.100.)J=31
      IF(T.GE.105.)J=46
      IF(T.GE.110.)J=61
      IF(T.GE.115.)J=76
      IF(T.GE.120.)J=91
      IF(T.GE.125.)J=106
      IF(T.GE.130.)J=121
      JJ=J+14
      W=15.
      DO 5 I=J,JJ
      W=W+1.
      IF(AW.GT.W)GO TO 5
      GO TO 6
    5 CONTINUE
      I=JJ
    6 DIF1=AW-W
      J=I-1
      FK=(TM(I)-TM(J))*DIF1+TM(I)
      FK1=(TM(I+15)-TM(J+15))*DIF1+TM(I+15)
      IT=(T+.00001)/5.
      DIF2=T-IT*5
      IF(T.GE.135.)DIF2=T-130.
      IF(T.LT.90.)DIF2=T-90.
      FK=FK+(FK1-FK)*DIF2/5.
      IF(X(6).LT..0001)GO TO 17
      FKN=(TN(I)-TN(J))*DIF1+TN(I)
      FK1=(TN(I+15)-TN(J+15))*DIF1+TN(I+15)
      FKN=FKN+(FK1-FKN)*DIF2/5.
      FK=FK+(FKN-FK)*X(6)/.0425
   17 FK=FK/1000.
      FMKM=1./(VI-FK*X(1))
      RETURN
   20 FMKM=0.0
      RETURN
      END

      FUNCTION V  IDEAL(T,X)
      DIMENSION X(10)
      V=0
      J=0
      IF(X(6).GT..0001.AND.T.GT.115.)J=1
      DO 10 I=1,8
      IF(X(I).LE..000001)GO TO 10
      IF(J.GT.0.AND.I.EQ.6)GO TO 10
      V=V+X(I)/SAT(T,I)
   10 CONTINUE
      IF(J.EQ.1)V=V+X(6)/SATN2(T)
      VIDEAL=V
      RETURN
      END

      FUNCTION SATN2(T)
      IF(T.LT.115.)GO TO 1
      DELT=(T-115.)
      SATN2=SAT(115.,6)+DELT*(SAT(115.05,6)-SAT(114.95,6))/.1
      RETURN
    1 SATN2=SAT(T,6)
      RETURN
      END
      FUNCTION SAT(T,I)
      UNITS ARE DEG K AND MOLES/LITER
      DIMENSION A(7,8)
      DATA((A(I),I=1,7)=190.555,10.16,18.65812322,6.712030737,
     1-.9472019702,0.0,0.0)
      DATA((A(I),I=8,14)=305.33,
     1     6.86,12.55205121,13.43284373,-19.00461066,11.07715985,0.0)
      DATA((A(I),I=15,21)=369.82,5.,8.684458671,18.04085714,-29.46261356
     1,16.43559114,0.0)
      DATA((A(I),I=22,28)=425.16,3.92,
     1                       7.286062567,11.96307859,-19.87591962,
     211.60211932,0.0)
      DATA((A(I),I=29,35)=408.13,3.8,
     1                       7.657535400,8.145251283,-13.10582462,
     28.145894091,0.0)
      DATA((A(I),I=36,42)=126.2,11.21,19.39216835,26.01408462,-39.497587
     191,23.32977312,0.0)
      DATA((A(I),I=43,49)=469.6,3.285,-.0362004993,59.00202990,
     1-93.44193819,43.66780833,0.0)
      DATA((A(I),I=50,56)=460.39,3.271,2.946310456,35.50770979,
     1-57.41242993,28.15898339,0.0)
      IF(T.GT.A(1,I))GO TO 1
      X=(1.-T/A(1,I))
      SAT=(A(2,I)+A(3,I)*X**(.35)+A(4,I)*X+A(5,I)*X**(4./3.)
     1+A(6,I)*X**(5./3.))
      RETURN
    1 SAT=1.E+20
      RETURN
      END
```

Appendix E. Program Listing for the Cell Model

```
  SUBROUTINE ECKNON(PIN,DOUT,TIN,Q)
  MAIN: ECKERT-RENON DENSITY MODEL                                  LNGD
                                                                    LNGD
                                                                    LNGD
     THIS PROGRAM IS DESIGNED FOR THE CALCULATION OF                LNGD
          LNG LIQUID DENSITIES ONLY AND WILL NOT                    LNGD
          COMPUTE DENSITIES ABOVE 160 K.                            LNGD
                                                                    LNGD
                                                                    LNGD
     THIS PROGRAM IS CALIBRATED SOLELY AGAINST DATA                 LNGD
          MEASURED BY                                               LNGD
               UNITED STATES DEPARTMENT OF COMMERCE                 LNGD
               NATIONAL BUREAU OF STANDARDS                         LNGD
               CRYOGENICS LABORATORY                                LNGD
               BOULDER, COLORADO                                    LNGD
                                                                    LNGD
                                                                    LNGD
                                                                    LNGD
   COMPONENT ID NUMBERS ARE                                         LNGD
     1 METHANE
     2 ETHANE
     3 PROPANE
     4 N-BUTANE
     5 I-BUTANE
     6 NITROGEN
                                                                    LNGD
                                                                    LNGD
                                                                    LNGD
                                                                    LNGD
  INPUT VARIABLES ARE
     PIN=PRESSURE IN ATMOSPHERES
     TIN=TEMPERATURE IN DEGREES KELVIN
     Q=MATRIX OF MOLE FRACTIONS OF COMPONENTS
  OUTPUT VARIABLE IS
     DOUT=DENSITY IN MOLES/LITER
  DIMENSION VHOLD(12),VPHOLD(12),Q(6)
  COMMON /RUN/ID(12),X(12),NAM(2,12),C12(12,12),R(12),Z(12),S(12),VSLNGD
 1(12),TS(12),US(12),SG(12),EP(12),LAM(12),NC,MW(12),AIJ(12,12),PST(LNGD
 212),TCT(12)                                                       LNGD
  COMMON /DAT/TBI(12),VBI(12),TBIM(12),VBIM(12),C(12),SGIM(12),SIM(1LNGD
 112),EPIM(12),PIM(12),SIN(12),VSIM(12),USIM(12),TSIM(12),DVBIM(12),PLNGD
 2D(12),PV(12),RHO(12),VBIMP(12),TTM(12),MWM,CNT1,CNT2,TOLD(12),INCRLNGD
 3(12),SWITCH,JPC,JPCS,JMIX,DENS,VEX,HEX,GEX,TMP,VMP,TP             LNGD
  COMMON/PAR/KIJ( 6, 6),AJI( 6, 6)                                  LNGD
  COMMON/UNITS/ITC,IPC,T,TMAX,DT,P,PMAX,DP,PS                       LNGD
  TYPE REAL MW,LAM,MWM,INCR,KIJ,MOL,LAMB
  TYPE INTEGER CNT1,CNT2,SWITCH,CODE
  P=PIN
  T=TIN
1 CALL ZERO1
  CALL INPUT(Q)
  IF(T.GT.(160.)) GO TO 19                                          LNGD
8 CALL PZERO(CTMX)                                                  LNGD
  MWM = 0                                                           LNGD
  DO 9 I = 1,NC                                                     LNGD
  MWM = MWM + (X(I)*MW(I))                                          LNGD
9 CONTINUE                                                          LNGD
```

```
   10 DO 11 I = 1,NC                                                    LNGD
      TBI(I) = T / TS(I)                                                LNGD
      CALL VOLUME(TBI(I),VBI(I),JPUR,NC)                                LNGD
      TBIM(I) = T / TSIM(I)                                             LNGD
      CALL VOLUME(TBIM(I),VBIM(I),JMIX,NC)                              LNGD
   11 CONTINUE                                                          LNGD
      VM =  0.0                                                         LNGD
      DO  12  I = 1,NC                                                  LNGD
      VM =  VM  + (X(I)*VBIM(I)*VSIM(I))                                LNGD
   12 CONTINUE                                                          LNGD
      TMP = ( T * 1.8) - (459.67)                                       LNGD
      DO 13 I = 1,NC                                                    LNGD
      VHOLD(I) = VBI(I)                                                 LNGD
      VFHOLD(I) = VBIM(I)                                               LNGD
      PP = (P*TS(I))/US(I)                                              LNGD
      VBIMP(I) = VBI(I)                                                 LNGD
      CALL PRES(PP,VBIMP(I),TBI(I),NC)                                  LNGD
      VBI(I) = VBIMP(I)                                                 LNGD
      PP = (P * TSIM(I)) / USIM(I)                                      LNGD
      VBIMP(I) = VBIM(I)                                                LNGD
      CALL PRES(PP,VBIMP(I),TBIM(I),NC)                                 LNGD
      VBIM(I) = VBIMP(I)                                                LNGD
   13 CONTINUE                                                          LNGD
      VMP = 0.0                                                         LNGD
      DO 14 I = 1,NC                                                    LNGD
      VMP = VMP + (X(I)*VBIMP(I)*VSIM(I))                               LNGD
      PO(I) = VBIMP(I) * VSIM(I)                                        LNGD
   14 CONTINUE                                                          LNGD
      DENS = MWM/VMP                                                    LNGD
      DOUT=DENS*1000./MWM
      RETURN
   19 DOUT=0.0
      RETURN
      END
      SUBROUTINE ZERO1
      COMMON /RUN/A(361)                                                ZERO
      COMMON /DAT/B(224)                                                ZERO
      DO 1 I = 1,361                                                    ZERO
    1 A(I) = 0.0                                                        ZERO
      DO 2 I = 1,224                                                    ZERO
    2 B(I) = 0.0                                                        ZERO
      RETURN                                                            ZERO
      END                                                               ZERO
      SUBROUTINE VOLUME(T,V,J,NC)                                       VOL
      TR = T                                                            VOL
      IF(TR.GT.(1.00)) GO TO 4                                          VOL
      V = 0.5                                                           VOL
    1 VT = (1.0) + (0.1*TR*V**(4.0))                                    VOL
      ERR = (1.0) - (V/VT)                                              VOL
      TEST = ABS(ERR)                                                   VOL
      IF(TEST.LE.(0.00001)) GO TO 2                                     VOL
      V = VT                                                            VOL
      GO TO 1                                                           VOL
    2 V = V**(3.0)                                                      VOL
    3 RETURN                                                            VOL
    4 V = ((((((10.06600 *TR)-24.79837)*TR)+23.260722)*TR)-5.686880)    VOL
      GO TO 3                                                           VOL
      END                                                               VOL
      SUBROUTINE INPUT(Q)
      DIMENSION NNO( 6),SIGM( 6),EPSI( 6),LAMB( 6),NAME(2, 6),SNO( 6),MOIN
     1L( 6),CT( 6),TCH( 6),VCH( 6),ECH( 6),AR( 6),AZ( 6),Q(6)
      COMMON /RUN/ID(12),X(12),NAM(2,12),C12(12,12),P(12),Z(12),S(12),VSIN
     1(12),TS(12),US(12),SG(12),EP(12),LAM(12),NC,MW(12),AIJ(12,12),PST(IN
     212),TCT(12)                                                       IN
      COMMON /DAT/TBI(12),VBI(12),TBIM(12),VBIM(12),C(12),SGIM(12),SIM(1IN
     112),EPIM(12),PIM(12),SIN(12),VSIM(12),USIM(12),TSIM(12),DVBIM(12),PIN
     2D(12),PV(12),RHO(12),VBIMP(12),TTM(12),MWM,CNT1,CNT2,TOLD(12),INCRIN
     3(12),SWITCH,JPC,JPCS,JMIX,DENS,VEX,HEX,GEX,TMP,VMP,TP             IN
      COMMON/PAR/KIJ( 6, 6),AJI( 6, 6)                                  IN
      TYPE REAL  MW,LAM,MWM,INCR,KIJ,MOL,LAMB
      TYPE INTEGER CNT1,CNT2,SWITCH
      DATA SIGM/                                                        IN
     *0.991000,1.029000,1.155000,1.278000,1.388752,1.392995/            IN
      DATA EPSI/                                                        IN
     *0.640000,0.909000,1.69800,2.237000,2.705262,2.545907/             IN
      DATA LAMB/                                                        IN
     *1.053604,0.986325,1.227117,1.408519,1.473346,1.461676/            IN
      DATA  MOL/                                                        IN
     *28.01600,16.04200,30.06800,44.09400,58.12000,58.12000/            IN
      DATA  SNO/                                                        IN
     *10.00000,10.00000,10.00000,10.00000,10.00000,10.00000/            IN
      DATA CT/                                                          IN
     *126.0600,190.5600,305.4300,369.8200,425.1600,408.0300/            IN
      DATA  TCH/                                                        IN
     *112.7699,170.9645,256.8311,294.7255,340.7867,322.6109/            IN
      DATA  VCH/                                                        IN
     *26.01846,29.04010,40.88188,54.60301,68.72075,69.44272/            IN
      DATA  ECH/                                                        IN
     *1393.000,1977.000,3695.000,4867.000,5886.652,5539.895/            IN
      DATA   AR/                                                        IN
     *1.000000,1.000000,1.000000,1.000000,1.000000,1.000000/            IN
      DATA   AZ/                                                        IN
     *10.00000,10.00000,10.00000,10.00000,10.00000,10.00000/            IN
      DO4 I=2,6
    4 X(I)=Q(I-1)
      X(1)=Q(6)
      NC=0
      DO 1 I=1,6
      IF(X(I).LE.0.0)GO TO 1
      NC=NC+1
      X(NC)=X(I)
      ID(NC)=I
    1 CONTINUE
      DO 2 I = 1,NC                                                     IN
      J = ID(I)                                                         IN
      R(I) = AR(J)                                                      IN
      Z(I) = AZ(J)                                                      IN
      S(I) = SNO(J)                                                     IN
      TS(I)= TCH(J)                                                     IN
      US(I)= ECH(J)                                                     IN
      SG(I) = SIGM(J)                                                   IN
      TCT(I) = CT(J)                                                    IN
      EP(I) = EPSI(J)                                                   IN
      LAM(I) = LAMB(J)                                                  IN
      VS(I) = VCH(J)                                                    IN
      MW(I) = MOL(J)                                                    IN
    2 CONTINUE                                                          IN
      DO 3 I = 1,NC                                                     IN
      DO 3 J = 1,NC                                                     IN
      M = ID(I)                                                         IN
      L = ID(J)                                                         IN
      C12(I,J) = KIJ(M,L)                                               IN
      C12(J,I) = KIJ(L,M)                                               IN
      AIJ(I,J) = AJI(M,L)                                               IN
      AIJ(J,I) = AJI(L,M)                                               IN
    3 CONTINUE                                                          IN
      RETURN                                                            IN
      END                                                               IN
      SUBROUTINE PRES(A,B,C,NC)                                         PRES
      TYPE REAL H,P,V,T,K1,K2,K3,VT,PT,K4
      P = A                                                             PRES
      V = B                                                             PRES
      T = C                                                             PRES
      H=.01
      IF(H.GT.P) H = P                                                  PRES
      ASSIGN 3 TO KK                                                    PRES
    1 CALL BETA(P,K1,T,V,NC)                                            PRES
      K1 = H * K1                                                       PRES
      VT=V+K1/2.
      PT=P+H/2.
      CALL BETA(PT,K2,T,VT,NC)                                          PRES
      K2 = K2 * H                                                       PRES
      VT=V+K2/2.
      CALL BETA(PT,K3,T,VT,NC)                                          PRES
      K3 = K3 * H                                                       PRES
      PT = P + H                                                        PRES
      VT = V + (  K3)                                                   PRES
      CALL BETA(PT,K4,T,VT,NC)                                          PRES
      K4 = K4 * H                                                       PRES
      V=V+(K1+2.*K2+2.*K3+K4)/6.
      P = P - H                                                         PRES
      IF(P.EQ.(0.0)) GO TO 4                                            PRES
      IF(P.LT.(0.0)) GO TO 2                                            PRES
      GO TO 1                                                           PRES
    2 GO TO KK , (3,4)                                                  PRES
    3 P = P + H                                                         PRES
      H = P                                                             PRES
      ASSIGN 4 TO KK                                                    PRES
      GO TO 1                                                           PRES
    4 A = P                                                             PRES
      B = V                                                             PRES
      C = T                                                             PRES
      RETURN                                                            PRES
      END                                                               PRES
      SUBROUTINE PZERO(TRT)                                             PZER
      COMMON /RUN/ID(12),X(12),NAM(2,12),C12(12,12),R(12),Z(12),S(12),VSPZER
     1(12),TS(12),US(12),SG(12),EP(12),LAM(12),NC,MW(12),AIJ(12,12),PST(PZER
     212),TCT(12)                                                       PZER
      COMMON /DAT/TBI(12),VBI(12),TBIM(12),VBIM(12),C(12),SGIM(12),SIM(1PZER
     12),EPIM(12),PIM(12),SIN(12),VSIM(12),USIM(12),TSIM(12),DVBIM(12),PPZER
     2D(12),PV(12),RHO(12),VBIMP(12),TTM(12),MWM,CNT1,CNT2,TOLD(12),INCRPZER
     3(12),SWITCH,JPC,JPCS,JMIX,DENS,VEX,HEX,GEX,TMP,VMP,TP             PZER
      COMMON/PAR/KIJ( 6, 6),AJI( 6, 5)                                  PZER
      COMMON /UNITS/ITC,IPC,T,TMAX,DT,P,PMAX,DP,PS                      PZER
      TYPE REAL  MW,LAM,MWM,INCR,KIJ,MOL,LAMB
      TYPE INTEGER CNT1,CNT2,SWITCH
      IF(NC.EQ.1) TRT = T/TCT(1)                                        PZER
      IF(NC.GT.1) CALL TCM(TRT)                                         PZER
      IF(NC.GT.1) TRT = T/TRT                                           PZER
      IF(NC.EQ.1) CALL PURE(TRT,TRT,R(1),RXX)                           PZER
      DO 1 I = 1,NC                                                     PZER
      TCXX = T/TCT(I)                                                   PZER
      IF(NC.GT.1) CALL PURE(TCXX,TRT,R(I),RTR)                          PZER
      JPC = 0                                                           PZER
      IF(TRT.GT.(.87)) JPC = 2                                          PZER
      IF(TRT.GT.(1.0)) JPC = 1                                          PZER
      IF(NC.EQ.1) RTR = RXX                                             PZER
      THERE ARE SEVERAL OTHER FORMS OF THESE EQUATIONS                  PZER
      REFER TO ORIGINAL ARTICLES FOR VALUES TO USE                      PZER
      S(I) = RTR  * Z(I) - 2. * RTR  + 2.                               PZER
      SIM(I) = S(I)                                                     PZER
      SG(I) = (VS(I)/RTR ) **(1./3.)                                    PZER
      EP(I) = US(I) / S(I)                                              PZER
      C(I) = LAM(I) * (2176./((185.6)*(1.98726)))                       PZER
      TTM(I) = TS(I)                                                    PZER
      TOLD(I) = TS(I)                                                   PZER
      INCR(I) = (20.0)                                                  PZER
    1 CONTINUE                                                          PZER
      JFUR = 0                                                          PZER
      CNT1 = 1                                                          PZER
      CNT2 = 1                                                          PZER
      JMIX = 0                                                          PZER
    2 DEN = 0                                                           PZER
      DO 3 I = 1,NC                                                     PZER
      DEN = DEN + (X(I) * SIM(I))                                       PZER
    3 CONTINUE                                                          PZER
      DO 4 I = 1,NC                                                     PZER
      PIM(I) = (X(I) * SIM(I)) / DEN                                    PZER
    4 CONTINUE                                                          PZER
      DO 6 I = 1,NC                                                     PZER
      SGIM(I) = 0.0                                                     PZER
      DO 6 J = 1,NC                                                     PZER
      M = I                                                             PZER
      N = J                                                             PZER
      IF(I.GT.J) M = J                                                  PZER
      IF(I.GT.J) N = I                                                  PZER
      IF(I.EQ.J) GO TO 5                                                PZER
      TRUOX = (AIJ(N,M)/(T/TTM(I)))                                     PZER
      IF(TRUDX.LT.(-180.0)) GO TO 5                                     PZER
      SGIM(I) = SGIM(I) +((PIM(J) *(((SG(I)**(1./3.) + SG(J)**(1./3.))  PZER
     1/(2.0)) **3))* (AIJ(M,N) * EXP(AIJ(N,M)/(T/TTM(I)))))             PZER
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      GO TO 6                                                           PZER
    5 SGIM(I) = SGIM(I) +(PIM(J) *(((SG(I)**(1./3.) + SG(J)**(1./3.))  PZER
     1/(2.0)))**3 )                                                     PZER
    6 CONTINUE                                                          PZER
      DEN = 0.0                                                         PZER
      DO 7 I = 1,NC                                                     PZER
      DEN = DEN + (PIM(I)* SGIM(I)* SGIM(I))                            PZER
    7 CONTINUE                                                          PZER
      DO 8 I = 1,NC                                                     PZER
      SIN(I) =(S(I) * (SGIM(I)**(2.))) / DEN                            PZER
    8 CONTINUE                                                          PZER
      DO 9 I = 1,NC                                                     PZER
      TEST = (1.0) - (SIM(I) / SIN(I))                                  PZER
      TEST = ABS (TEST)                                                 PZER
      IF(TEST.GT.(0.00001)) GO TO 10                                    PZER
    9 CONTINUE                                                          PZER
      GO TO 12                                                          PZER
   10 DO 11 I = 1,NC                                                    PZER
      SIM(I) =(SIM(I) + SIN(I)) /(2.0)                                  PZER
   11 CONTINUE                                                          PZER
      CNT1 = CNT1 + 1                                                   PZER
      IF(CNT1.GT.250) GO TO 12                                          PZER
      GO TO 2                                                           PZER
   12 DO 14 I = 1,NC                                                    PZER
      SIM(I) = SIN(I)                                                   PZER
      EPIM(I) = 0.0                                                     PZER
      DO 14 J = 1,NC                                                    PZER
      K = I                                                             PZER
      L = J                                                             PZER
      IF(J.LT.I) K = J                                                  PZER
      IF(J.LT.I) L = I                                                  PZER
      IF(I.EQ.J) GO TO 13                                               PZER
      TRUDX = C12(L,K) / (T/TTM(I))                                     PZER
      IF(TRUDX.LT.(-180.0)) GO TO 13                                    PZER
      EPIM(I) = EPIM(I) +((PIM(J) * SQRT(EP(I)*EP(J)))*                 PZER
     1(C12(K,L) * EXP((C12(L,K) /(T/TTM(I))))))                         PZER
      GO TO 14                                                          PZER
   13 EPIM(I) = EPIM(I) + (PIM(J) * SQRT(EP(I) * EP(J)))                PZER
   14 CONTINUE                                                          PZER
      ASSUME NUMBER OF MOLS OF MIXTURE = 1.0                            PZER
      DO 15 I = 1,NC                                                    PZER
      VSIM(I) = R(I) * (SGIM(I)**(3.0))                                 PZER
      USIM(I) = SIM(I) * EPIM(I)                                        PZER
      TSIM(I) = USIM(I) / ((1.98726) * C(I))                            PZER
   15 CONTINUE                                                          PZER
      DO 16 I = 1,NC                                                    PZER
      TEST = (1.0) - (TSIM(I)/TTM(I))                                   PZER
      TEST = ABS(TEST)                                                  PZER
      IF(TEST.GT.(0.00001)) GO TO 17                                    PZER
   16 CONTINUE                                                          PZER
      RETURN                                                            PZER
   17 DO 20 I = 1,NC                                                    PZER
      IF(TSIM(I) - TTM(I))18,20,19                                      PZER
   18 TNEW = TTM(I) - INCR(I)                                           PZER
      IF(TNEW.EQ.TOLD(I)) INCR(I) = INCR(I)/ (2.0)                      PZER
      IF(TNEW.EQ.TOLD(I)) GO TO 18                                      PZER
      TOLD(I) = TTM(I)                                                  PZER
      TTM(I) = TNEW                                                     PZER
      GO TO 20                                                          PZER
   19 TNEW = TTM(I) + INCR(I)                                           PZER
      IF(TNEW.EQ.TOLD(I)) INCR(I) = INCR(I) / (2.0)                     PZER
      IF(TNEW.EQ.TOLD(I)) GO TO 19                                      PZER
      TOLD(I) = TTM(I)                                                  PZER
      TTM(I) = TNEW                                                     PZER
   20 CONTINUE                                                          PZER
      CNT2 = CNT2 + 1                                                   PZER
      IF(CNT2.GT.250) RETURN                                            PZER
      GO TO 2                                                           PZER
      END                                                               PZER

      SUBROUTINE PURE(TZ,T,Z,R)                                         PURE
      DIMENSION A(15)                                                   PURE
      DATA A/.9184780,-.1530647,-.1090050,.8073883,1.441803,            PURE
     1-10.85944,-6.041687,51.26758,.9062500,-108.9805,28.88672,         PURE
     2106.1406,-45.78125,-38.43750,20.56250/                            PURE
      IF(TZ.LT.(.8653525)) R = Z                                        PURE
      IF(TZ.LT.(.8653525)) GO TO 2                                      PURE
      IF(T.LT.(.8653525)) R = Z                                         PURE
      IF(T.LT.(.8653525)) GO TO 2                                       PURE
      IF(T.GT.(1.0)) TA = 1.0                                           PURE
      IF(T.LE.(1.0)) TA = T                                             PURE
      R = 0.0                                                           PURE
      TT = (TA - (.9267292)) / (.7267517E-01)                           PURE
      DO 1 K = 1,14                                                     PURE
      R = R + A(16-K)                                                   PURE
      R = R * TT                                                        PURE
    1 CONTINUE                                                          PURE
      R = R + A(1)                                                      PURE
    2 RETURN                                                            PURE
      END                                                               PURE

      SUBROUTINE BETA(P,DV,T,V,KK)                                      BETA
      DIMENSION C(11)
      DATA AF/0.11566564E+02/,BF/-0.53510144E+01/,CF/-0.74598207E-01/,  BETA
     1DF/0.67068653E+00/,EF/-0.11939887E+00/,AG/0.62721813E+01/,        BE
     2BG/0.47693365E+00/,CG/-0.15023080E+01/,DG/0.49837746E+00/,        B
     3EG/-0.42639183E-01/
      DATA C/-.118659822E+02,-.5509099E+00,.4172102E+01,-.8996686E+00,
     1-.1500376E+01,-.1958324E+00,-.2788988E+01,.5195283E+00,
     2.3734878E+01,.1361904E+00,.4671948E-01/
      F = AF +(BF*V)+(CF*V*V)+ (DF*V*V*V)+(EF*V*V*V*V)                  BETA
      IF(F.LT.(0.0)) GO TO 1                                            BETA
      F1 = (BF+(CF*V*2.     )+(DF*V*V*3.     )+(EF*V*V*V*4.     ))*     B
     1T*EXP(F)
      G = AG+(BG*V)+(CG*V*V)+(DG*V*V*V)+(EG*V*V*V*V)                    BETA
      IF(G.LT.(0.00)) GO TO 1                                           BETA
      G1 = (BG+(CG*V*2.     )+(DG*V*V*3.     +(EG*V*V*V*4. )     )) *EXP(G)
      G1 = -G1                                                          BETA
      DEN = F1 + G1                                                     BETA
      DV=1./DEN
      IF(DV.GT.(0.0).OR.DV.LT.(-1.     0)) GO TO 1                      BETA
      GO TO 2                                                           BETA
    1 B1 = C(1) + C(2)*T + C(3)*V                                       BETA
      B2 = C(4)*((V+C(5))**(2 ))* EXP((C(6))*((T+C(7))**(2 )))
      B3 = C(11) * (V+C(8))**(C(9))/(T**(C(10)))                        BETA
      DV = B1 + B2 + B3                                                 BETA
      DV=EXP(DV)
      DV = - DV                                                         BETA
    2 RETURN                                                            BETA
      END                                                               BETA
      SUBROUTINE TCM(TMC)                                               TCM
      TYPE REAL   MW,LAM,MWM,INCR,KIJ,MOL,LAMB,NUM
      TYPE INTEGER CNT1,CNT2,SWITCH
      DIMENSION VCI( 6),TH(12)                                          TCM
      COMMON /RUN/ID(12),X(12),NAM(2,12),C12(12,12),R(12),Z(12),S(12),VSTCM
     1(12),TS(12),US(12),SG(12),EP(12),LAM(12),NC,MW(12),AIJ(12,12),PST(TCM
     212),TCT(12)                                                       TCM
      COMMON /DAT/TBI(12),VBI(12),TBIM(12),VBIM(12),C(12),SGIM(12),SIM(1TCM
     12),EPIM(12),PIM(12),SIN(12),VSIM(12),USIM(12),TSIM(12),DVBIM(12),PTCM
     2D(12),PV(12),RHO(12),VBIMP(12),TTM(12),MWM,CNT1,CNT2,TOLD(12),INCRTCM
     3(12),SWITCH,JPC,JPCS,JMIX,DENS,VEX,HEX,GEX,TMP,VMP,TP             TCM
      COMMON/PAR/KIJ( 6, 6),AJI( 6, 6)                                  TCM
      COMMON/UNITS/ITC,IPC,T,TMAX,DT,P,PMAX,DP,PS                       TCM
      DATA VCI/ 1.44,1.59,2.27,3.18,4.03,4.21/                          TCM
      DO 1 I = 1,NC                                                     TCM
      J = ID(I)                                                         TCM
      V = VCI(J)**(2./3.)                                               TCM
      TH(I) = X(I) * V                                                  TCM
    1 CONTINUE                                                          TCM
      TTZ = 0.0                                                         TCM
      DO 2 I = 1,NC                                                     TCM
      TTZ = TTZ + TH(I)                                                 TCM
    2 CONTINUE                                                          TCM
      DO 3 I = 1,NC                                                     TCM
      TH(I) = TH(I) / TTZ                                               TCM
    3 CONTINUE                                                          TCM
      SUM1 = 0.0                                                        TCM
      SUM2 = 0.0                                                        TCM
      K = NC - 1                                                        TCM
      DO 5 I = 1,K                                                      TCM
      L = I + 1                                                         TCM
      DO 4 J = L,NC                                                     TCM
      TTZ = (TCT(I)-TCT(J))/(TCT(I)+TCT(J))                             TCM
      TTZ= ABS(TTZ)                                                     TCM
      T12 = (((((((TTZ*(-3.038))+(5.443))*TTZ)+(-1.343))*TTZ)           TCM
     1 + (0.287))*TTZ) - (.0076)                                        TCM
      T12 = T12*(TCT(I) + TCT(J)) * (0.9)                               TCM
      SUM2 = SUM2 + ((2.)*TH(I)*TH(J)*T12)                              TCM
    4 CONTINUE                                                          TCM
      SUM1 = SUM1 + (TH(I)*TCT(I)*(1.8))                                TCM
    5 CONTINUE                                                          TCM
      TMC = SUM1 + SUM2 + (TH(NC)*TCT(NC)*(1.8))                        TCM
      V = 0.0                                                           TCM
      DO 6 I = 1,NC                                                     TCM
      J = ID(I)                                                         TCM
      TH(I) = X(I) * VCI(J)                                             TCM
      V = V + TH(I)                                                     TCM
    6 CONTINUE                                                          TCM
      DO 7 I = 1,NC                                                     TCM
      TH(I) = TH(I) / V                                                 TCM
    7 CONTINUE                                                          TCM
      TDM=0.0
      DO 9 I = 1,NC                                                     TCM
      DO 8 J = 1,NC                                                     TCM
      M = ID(I)                                                         TCM
      N = ID(J)                                                         TCM
      NUM = (VCI(M)**(1./3.)) * (VCI(N)**(1./3.))                       TCM
      NUM = SQRT(NUM)                                                   TCM
      DEN = (0.5)*((VCI(M)**(1./3.))+(VCI(N)**(1./3.)))                 TCM
      NUM = NUM / DEN                                                   TCM
      NUM = NUM**(3.)                                                   TCM
      AKIJ = (1.0) - NUM                                                TCM
      TCIJ = (1.0 - AKIJ) * SQRT(TCT(I)*TCT(J)*1.8*1.8)                 TCM
      TDM=TDM+TH(I)*TH(J)*TCIJ
    8 CONTINUE                                                          TCM
    9 CONTINUE                                                          TCM
      TCMP=TDM+10.
      ICT = 0                                                           TCM
      TPO=TDM+10.
   10 TR = (T*1.8)/TCMP                                                 TCM
      NUM = (2901.01) -((5738.92)*TR) +((2849.85)*TR*TR)                TCM
     1 + ((1.74127)/ (1.01 - TR))                                       TCM
      NUM = NUM * (TR - (1.0))                                          TCM
      IF(NUM.LT.(-180.)) DD = 0                                         TCM
      IF(NUM.LT.(-180.)) GO TO 11                                       TCM
      DD = EXP(NUM)                                                     TCM
         THE STATEMENT ABOVE MAY RESULT IN AN UNDERFLOW SENSE LIGHT     TCM
           ON SOME OPERATING SYSTEMS WHEN THE NUMBER NUM IS A LARGE     TCM
           NEGATIVE NUMBER. THE LARGE NEGATIVE VALUE IS PROPER AND      TCM
           THE CORRECT ANSWER FOR DD IS ZERO.                           TCM
   11 TCMP = TDM + ((TMC-TDM)*DD)
      TEST = (1.0) - (TCMP/TPO)                                         TCM
      TEST = ABS(TEST)                                                  TCM
      IF(TEST.LT.(.0001)) GO TO 12                                      TCM
      ICT = ICT + 1                                                     TCM
      IF(ICT.GT.250) GO TO 12                                           TCM
      TPO = TCMP                                                        TCM
      GO TO 10                                                          TCM
   12 TMC = TCMP/(1.8)                                                  TCM
      RETURN                                                            TCM
      END                                                               TCM

      SUBROUTINE BLOCK
      TYPE REAL KIJ,AJI
      DIMENSION KIJ(6,6),AJI(6,6)
      COMMON /PAR/ KIJ,AJI                                              DATA
      DATA KIJ/                                                         DATA
     *0.000000,.293E-07,.988E-07,.584E-06,0.001000,0.001000,1.088508,   DATA
     *0.000000,.0537605,.744E-06,.238E-08,.154E-05,1.088264,1.029639,   DATA
     *0.000000,.403E-07,.224E-06,.261E-06,.9906540,1.139564,1.010192,   DATA
     *0.000000,.440E-07,.495E-07,0.995000,1.337262,.9867502,.9688072,   DATA
     *0.000000,.310E-05,0.995000,1.121902,1.016260,.9992935,.9435220,   DATA
     *0.000000/                                                         DATA
      DATA AJI/                                                         DATA
     *0.000000,.161E-04,.988E-06,.448E-05,0.001000,0.001000,1.014967,   DATA
     *0.000000,.0002462,.336F-06,.998E-06,.0000297,1.007314,1.008772,   DATA
     *0.000000,.603E-05,.0000225,.666E-06,1.001711,1.010832,1.001911,   DATA
     *0.000000,.622E-05,.280E-05,0.995000,1.027909,1.003225,.9987213,   DATA
     *0.000000,.317E-05,0.995000,1.015870,1.005915,1.001421,.9968974,   DATA
     *0.000000/                                                         DATA
      RETURN
      END                                                               DATA
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16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

Four mathematical models of the equation of state for LNG like mixtures are compared. Each model has been optimized to the same experimental data set. The experimental data consist of over 175 new PVTx data points taken in this laboratory. The objective of the study was to obtain a mathematical model which would predict LNG densities to within 0.1% of the true value. The extent to which the objective has been achieved is not clear at this time. Additional experimental data are needed to resolve some discrepancies between the present data and all models investigated to date. Computer program listings for all four models are presented.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)*

Computer program; density; equation of state; LNG; mixtures; PVTx.

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